PARTIAL OXIDATION OF ISOBUTANE

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PREFACE

The effect of temperature, initial reactant concentration and contact time on the partial oxidation of isobutane has been studied. The rate equation, product distribution and reaction mechanism are presented.

The author wishes to extend the deepest gratitude to his parents and his brothers.

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TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

CHAPTER I

INTRODUCTION

The slow and explosive oxidation of hydrocarbons with oxygen has been the subject of a great number of investigations for over fifty years. And despite the large volume of published information, our knowledge of oxidation of even simple hydrocarbons is still far from complete. This is partly due to the fact that the oxidation reaction is markedly sensitive to experimental conditions, particularly to the nature of the surface of the reaction vessel, the influence of impurities, and the effect of temperature.

In oxidation of hydrocarbons there are at least three areas of interest to investigators:

a- Stable oxidation region, cool preflame, in which slow partial oxidation occurs and luminescence may or may not occur in the oxidation.

b- The cool flame region, evidenced by high rates of partial oxidation.

c- Two stage ignition, leading to complete reaction.

Following earlier observations by Perkin et al (20), the cool flame phenomenon in hydrocarbon oxidation was studied systematically by Prettre et al (21). Townsend et al (33) studied extensively flame propagation through cold mixtures.

Two stage ignition consists of an induction period, t_1, from the beginning of the reaction to the appearance of cool flame

and t_2 from start of cool flame to onset of violent explosion.

The source of luminosity of the cool flame region has been firmly established as emanating from excited formaldehyde molecules (9). Cool flames do not occur in the oxidation of methane or ethane but are found in oxidation of rich mixtures of higher paraffins.

The temperature range in which cool flame phenomena occur begins at about 280°C. and extends up to about 420°C.

In the temperature range of 350 to 400°C., the range between low and high temperature oxidation of hydrocarbons, the negative temperature coefficient has also been observed. This abnormality in the reaction rate, a decrease rather than increase in the reaction rate and rate constant with increase in temperature, has been studied extensively (15) and much speculation concerning this phenomenon has been advanced but no generally acceptable explanation is yet available.

Surface and surface to volume ratios have a marked effect on the partial oxidation of hydrocarbons. Surface is generally known to have an inhibiting effect on the reactions by destruction of free radicals. Even though free radicals can be destroyed both homogeneously and heterogeneously, surface destruction is more efficient than gas phase destruction. Therefore, an increase in surface to volume ratio should yield a decreased reaction rate. This has been observed experimentally (18).

Ridge (22) has used He, Ar, N_2, and CO_2 to study the effect of inert gases in isobutane oxidation. The result was that the addition of inert gases systematically reduced the induction period (time required for the rate of pressure rise to reach 0.5 mm/min.).

Ridge suggests that the length of induction period is determined by the rate of destruction of an active intermediate at the walls of the reaction vessel.

The oxidation of hydrocarbons becomes a complex process with many factors involved in its course of reaction. But despite such complexities there is general agreement in some aspects of hydrocarbon oxidation among all investigators. One is that the oxidation has the characteristics of a degenerate branching chain reaction as exemplified by the observation of the sensitivity of the reaction to surface conditions, added inert gases, inhibitors and catalysis. It is also generally agreed that the active particles responsible for chain propagation are free radicals or atoms and the presence of alkyl, alkoxy, alkylperoxy, hydroperoxyl radicals and oxygen atoms has been postulated.

Semenov (25) in 1930-1934 was able to explain some of the features of slow oxidation in terms of branched chain reactions of degenerate or delayed type. Degenerate branching differs from other forms of branching in that the primary chain is unbranched and the additional centers are produced by side reactions of products of the primary chain. Degenerate branching is the result of an intermediate, but the identity of the intermediate is not clearly known yet.

Norrish (17) suggests that aldehydes formed lead to degenerate branching while Walsh (35) believes that below 350°C. the important intermediates are hydroperoxides. Other possibilities, such as the formation of olefins from saturated hydrocarbons, have also been considered in recent years. In general the importance of the

above intermediates in a given reaction can be classified as follows:

I- Temperatures below 350°C.

  a- Aldehydes

  b- Hydroperoxides

II- Temperatures above 350-400°C.

  a- Aldehydes

  b- Hydrocarbon radicals leading to olefins.

Hydroperoxides are very sensitive to temperature and therefore are unstable at high temperatures.

The objective of this investigation was to study the mechanism, rate and product distribution of the partial oxidation of isobutane. The experimental work covers a wide range of operating variables and provides an adequate scope from which the theory has been examined and developed. Isobutane was selected because little attention has been paid to it, and it is the logical precursor to an understanding of combustion of higher branch - chain hydrocarbons which are of more practical interest.

CHAPTER II

SURVEY OF LITERATURE

ISOBUTANE OXIDATION

Study of the partial oxidation of isobutane and in particular the rate and mechanism of this reaction has received little or no direct investigation.

Pease (18) in 1929 made some experiments in a flow system to study the wall effect on partial oxidation of isobutane, n-butane and propane. He concluded that the wall has a predominately negative catalytic effect. He explains that excited molecules of products are deactivated by the wall instead of transferring their excitation energy to fresh molecules of reactants. Addition of alkali halide solutions to the wall, for their poisoning effect, did not alter the rate in empty tubes but did have a positive effect in packed tubes. The conclusion was that the observed reaction is exclusively homogeneous in empty tubes.

Taylor (30) in his experiments found that the peroxides in isobutane oxidation were mainly hydrogen peroxide and tertiary butyl hydroperoxide. The appearance of tertiary butyl hydroperoxide has also been reported by Batten (2).

Addition of ozone to isobutane oxidation reaction accelerates the reaction and results in the formation of liquid products for temperatures below 265-275°C. For temperatures above 275°C. the reaction product goes to completion with or without addition of

ozone. Pease and others (19) have suggested that ozone might be the active intermediate responsible for chain branching during the slow oxidation of isobutane.

The mercury photosensitized oxidation of isobutane with five other hydrocarbons has been studied by Burgess and Robb(4). The temperature range was 0-400°C.

Rust and Vaughan (23) studied the effect of hydrogen bromide in isobutane oxidation. In the presence of HBr, branched chain compounds are converted chiefly to stable peroxides. The mechanism of the reaction appears to be a free radical chain, in which HBr functions both in initiation and propagation, and at temperatures up to 170°C. the important products were tertiary butyl hydroperoxide, di-tertiary-butyl peroxide and tertiary butyl alcohol.

Wright (36) has studied reaction of oxygen atoms with isobutane at 30°C. He concluded that the gas phase oxidation is homogeneous. The reaction mechanism has also been discussed in some detail by Wright.

CHAPTER III

EXPERIMENTAL WORK

A- EQUIPMENT:

Figure (1) shows the complete assembly and Figure (2) shows a schematic diagram of the isobutane oxidation apparatus.

Flow of isobutane from the isobutane cylinder is regulated by a Matheson No. 2043 M2 low pressure pancake regulator. Flow of oxygen from the oxygen cylinder is regulated by a Matheson No. 8 automatic two stage regulator. Matheson No. 116, ¼ inch needle valves were used to obtain fine control in both feeds.

Two Matheson No. 602 flowmeters were used to obtain the feed gas flow rate. The flowmeters were calibrated using a bubble soapmeter and the calibration curves are shown in Appendix III. The feed and reactor pressure were measured by mercury manometers.

Temperatures of the inlet gas mixture to reactor and the outlet from reactor were measured by chromel-constantan thermocouples. The axial reactor temperature was measured by a No. A1133 Wheelco iron-constantan thermocouple. Calibration curves for these thermocouples appear in Appendix III, and the position of thermocouples is shown in Figure (2).

A "student" potentiometer was used for thermocouple calibration. Later on, the temperatures were measured by Leeds and Northrup millivolt potentiometer, catalog No. 8686.

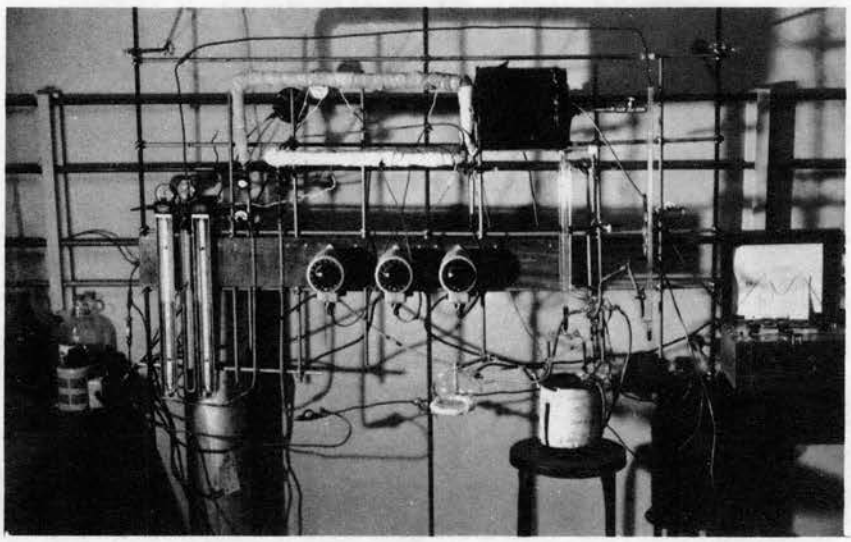

Figure 1

Isobutane Oxidation Assembly

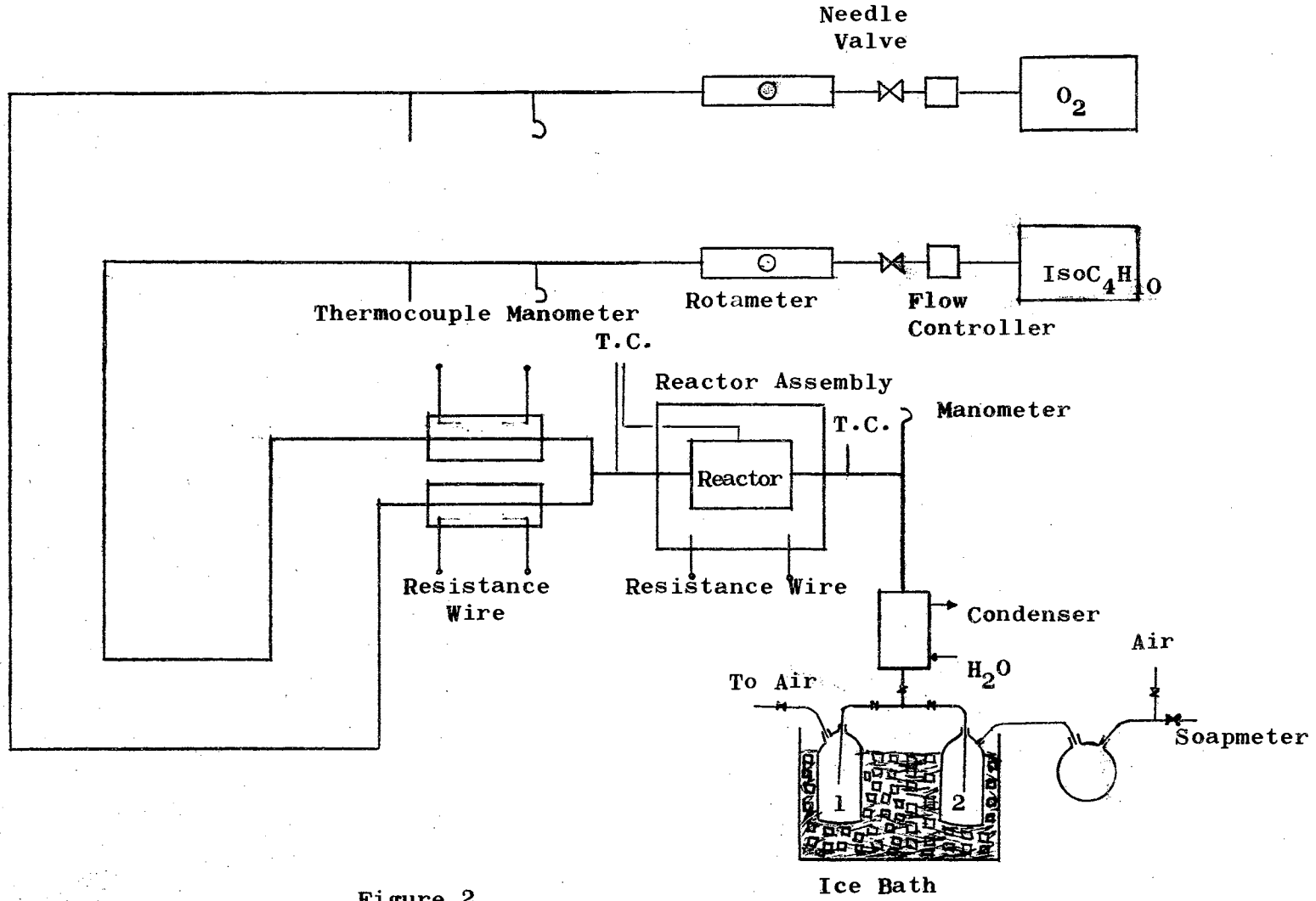

Figure 2

Schematic Diagram of Experimental Unit

The reactor was installed in a 10" x 10" x 10" oven. The oven was made of three layers which from inside to outside were: ¼ inch transite asbestos, 1½ inch glass wool, with an outer layer of ¼ inch plywood. Sufficient chromel-A gauge 24 resistance wire was mounted on the inner surface to maintain constant temperature at the desired levels in the oven. Feed gases prior to mixing were heated to about the desired temperature in two six foot lengths of ¼ inch diameter stainless steel tubes. The tubes were wrapped with chromel-A gauge 24 resistance wire. The wire was covered with beads and asbestos cloth.

Temperature regulation in the oven was achieved by five 110V AC powerstats.

A ¼ inch stainless steel flare was used for complete mixing of two feed streams. The reactor used in this experiment was a 1.5 inch long and 1.75 inch diameter stainless steel tube as shown in Figures (3,4). There was no initial treatment of the internal surface area of the reactor.

A cold water condenser and cold traps (two) in an ice bath were used to liquefy and collect the liquid products.

A bubble soapmeter was used to measure the flow of uncondensed gases from the reactor.

B- MATERIAL:

99.9% oxygen and 96.6% isobutane obtained from the Matheson Company were used. The isobutane impurities were 0.69% propane, 2.71% n-butane. The analysis was made by programmed gas chromatography.

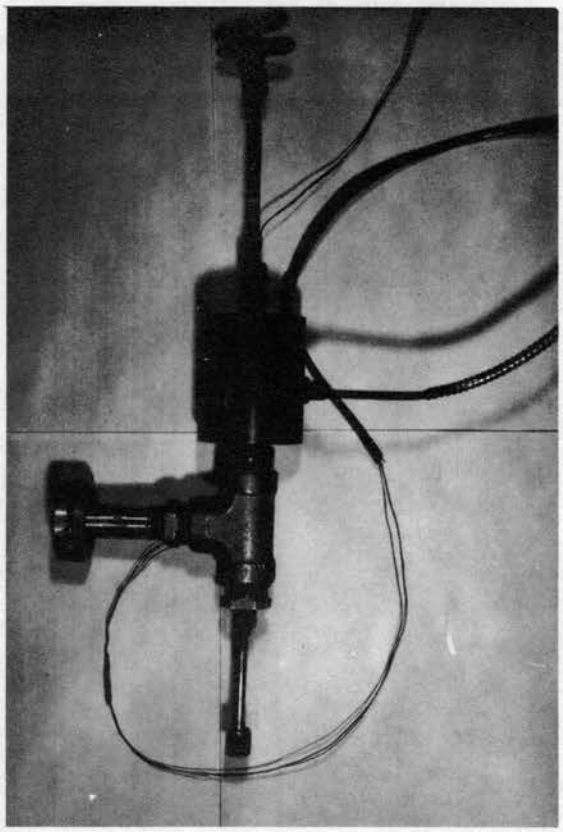

Figure 3

Reactor Assembly

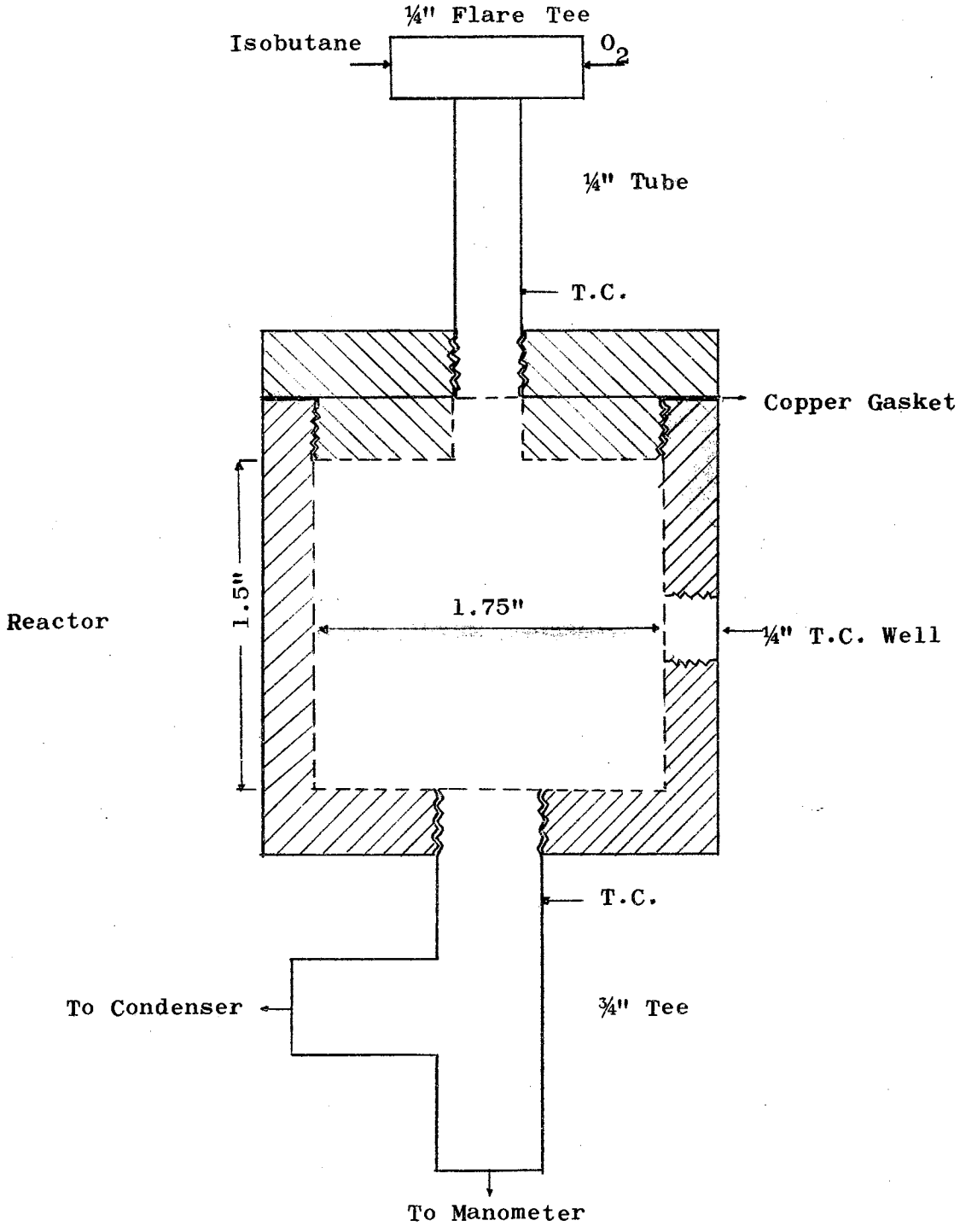

Figure 4

Schematic Diagram of Reactor

C- EXPERIMENTAL PROCEDURE:

To heat up the reactor and tubes, air was passed through the reactor for about eight to ten hours with the variacs at their maximum voltage. When the desired temperature was approached, the air valve was closed and the isobutane flow rate established at its desired level. The oxygen flow rate was then adjusted to its value.

In order to minimize the time required for preheating, the variacs were always left on with low voltages. In this way time was saved and no coke formation to plug the line was observed. Approximately four hours were required for each run to come to equilibrium. After the reactor temperature was steady, the product analysis for O_2, H_2, and CH_4, and carbon monoxide were reproducible, and the exit gas flow remained the same for two samples at fifteen minute intervals, the column was assumed to be at steady state. At this time an evacuated one liter gas sample bomb was connected to the exit gas stream of the first cold trap. When filled, it was disconnected from this stream and connected to the second cold trap. The second cold trap line was opened and the time recorded. A few minutes was allowed to remove the air from line and then the gas sample was opened. Each run took between one to three hours depending on the amount of liquid product collected in the cold trap. Usually three to four grams of liquid product was sufficient for the entire analysis.

During the run, at fifteen minute time intervals, the temperature and rate of gases leaving ice bath were measured.

Gas samples were directly taken from the line with a 5cc gas-tight Hamilton syringe and analyzed in an F & M Model 500 programmed temperature gas chromatograph for H_2, O_2, CH_4, and CO. Five minutes from the end of the run the gas sample bomb was disconnected and the alternate flow line was opened to let the gases out with no disturbance in reaction.

The liquid product collected in the cold trap was weighed and poured into a small sample bomb for liquid analysis.

D- PRODUCT ANALYSIS:

A combination of programmed gas chromatography and chemical methods was used to determine the reaction products and their composition in the product stream. A discussion of the programmed gas chromatography unit and a sample calculation for the product analysis are in Appendix IV.

Procedure:

D-1- Programmed gas chromatography-

The following columns were prepared to analyze the gas and most of the liquid products.

a- Molecular sieve column:

Type - 13X, 20-48 mesh, 6 ft.

Purpose - H_2, O_2, N_2, CH_4, CO separation

Condition - Col. temp. = 40°C, He=50cc/min., p = 10 psig,
block temp. = 160°C., current = 180 ma,
chart speed = 4 inches/min.

b- Di-butyl Phthalate column:

Type - D.B.P. on 28-35 mesh chromosorb P, 14 ft.

Purpose - Isobutane, n-butane, isobutylene, separation

Condition - Col. temp. = 30°C., He = 30 cc/min., p = 10 psig, current = 180 ma, block temp. = 160°C., chart speed = 4 inches/min.

c- Activated alumina column:

Type - Act. al., 20-48 mesh, 8 ft.

Purpose - Ethane, ethylene, propane, propylene, isobutylene separation

Condition - He = 15 cc/min., p = 14 psig, col. temp. = 75°C., current = 180 ma, chart speed = 4 inches/min., sample size = 1 cc and 5 cc.

d- Silica gel column:

Type - s.g. 20-48 mesh, 3½ ft.

Purpose - CO_2 separation.

Condition - He = 30 cc/min., p = 14 psig, block temp. = 160°C., col. temp. = 125°C., current 180 ma, chart speed = 4 inches/min.

Under above conditions CO_2 and ethylene form one peak. To get separate peaks, use He = 15 cc/min., col. temp. = 40-125°C. programmed on 4°C/min., if the concentration of ethylene is appreciable in exit gases.

e- Di-n-octyl Phthalate column:

Type - Di-n-O-P, chromosorb P, 30-60 mesh (unwashed), 13 ft. consisting of:

10 ft., Di-n-Octyle Phthalate supported on chromosorb P. 3 ft., Glycerol supported on Chromosorb P. One piece 13 ft. column was connected to inlet and

outlet He flow such that Glycerol side was inlet, in this way better separation is obtained. 30% by weight liquid Di-n-Octyl Phthalate was dissolved in acetone, mixed with Chromosorb P and acetone was removed by heating the mixture. The same procedure was used for Glycerol column preparation.

Purpose - To separate acetaldehyde, acetone, methanol, tertiary butyl alcohol, iso and normal butyl alcohol, and water.

Condition - He = 80 cc/min., P = 16 psig, block temp. = 300°C. current = 180 ma., col. temp. = 70-140°C. programmed at 4°C./min., chart speed = 2 inches/min.

D-II-Chemical Technique (29):

a- Formaldehyde Analysis-

Procedure - In 250 ml. flask containing 50 ml. of standard 0.1 M KCN and 5 cc of 30% $MgSO_4$ solution, add a known amount of sample (approximately 0.3 grams). Let stand for two to five minutes. Filter, add 1 gram of NH_4Cl, 2-3 drops of concentrated NH_4OH and a crystal of KI. Titrate the excess KCN with standard 0.05 N $AgNO_3$ until turbidity lasting two minutes is obtained.

Preparation of standard solution-

I- $AgNO_3$ - Dissolve 8.5 grams of silver nitrate in one liter of distilled water. Standardize against pure NaCl by titration using Chromate indicator.

$$AgNO_3 + NaCl \text{ ----} AgCl + NaNO_3$$

The end point corresponds to the formation of red silver chromate.

II- KCN solution

Dissolve 6.5 grams of KCN in one liter of distilled water. Standardize by titration against the standard solution of $AgNO_3$ prepared above.

$$2KCN + AgNO_3 \text{ ----} KNO_3 + K\,[Ag(CN)_2]$$

Titrate until solution becomes turbid.

Formaldehyde calculation - Weight percent of HCHO is calculated from the following relation:

$$\text{Wt.\% HCHO} = \frac{3.0}{\text{grams of sample}}\left[50N_{KCN} - 2(\text{ml.}AgNO_3 \times N_{AgNO_3})\right]$$

b- Acid Analysis-

Procedure - Into 50 ml. beaker place 20 ml. of distilled water and 2 drops of phenolphthalein solution. Titrate to a faint pink point with 0.01 NaOH solution. Add a known amount (about 0.5 grams) of sample. Titrate to the same point, use 10 microburrette. 0.01 NaOH solution preparation - Dissolve 0.4 grams of NaOH in one liter of distilled water. Standardize against potassium acid phthalate, $KCH_8H_4O_4$, using the phenolphthalein end point.

Acid calculation - Assuming that the acid is acetic acid :

$$\text{Wt.\% Acid} = \frac{(N_{NaOH})(\text{ml.Titrate})\ 60 \times 100}{1000\ (\text{grams of sample})} =$$

$$\frac{6(N_{NaOH})(\text{ml.Titrate})}{\text{grams of sample}}$$

c- Peroxide Analysis:

Weigh a sample estimated to have 0.25 grams of peroxide

and dissolve it in 25 ml. of glacial acetic acid. To this add 2 ml. of standard aqueous solution of potassium iodide, 5 drops of concentrated sulfuric acid, and a few pieces of dry ice. Allow to stand ten minutes. Titrate with 0.1 N solution of thiosulfate until end point is approached, as evidenced by the fading of the brown iodine color. Add 25 ml. of distilled water and 1 ml. of 2% starch solution. Continue titration until the familiar starch end point is reached. Gentle warming under a blanket of CO_2 may be used to accelerate the reaction.

$$ROOR + 2HI \text{-----} 2ROH + I_2$$

$$I_2 + 2S_2O_3 \text{-----} 2\bar{I} + S_4O_6^{++}$$

Preparation of 0.1 N Thiosulfate solution -

Dissolve about 25 grams of sodium thiosulfate and 0.1 gram Na_2CO_3 in one liter distilled water that has been boiled for several hours and allowed to cool. Standardize against pure crystalline iodine.

No peroxide was detected in these experiments.

CHAPTER IV

EXPERIMENTAL RESULTS

A total of 59 runs was made with the first 18 runs as exploratory work. The product distributions for major components are presented in graphical form in Figures (5) and (7) to (12). Table (2) shows the product distribution for all runs. The results of a typical run are given in Table (1). Runs 44, 47, 57, and 59 were duplicates of runs 41, 23, 51, and 40.

The range of variables covered in these experiments was as follows:

a- Temperature 350, 375, 400°C.

b- Initial oxygen concentration, 20, 30, 40%.

c- Contact time, 4-16 seconds, based on inlet feed gases to reactor. Only one set of data was obtained for 30% O_2 concentration and it was for 350°C. The product distribution at 375°C. and 40% oxygen concentration are shown in this chapter, and the remainder is presented in Appendix I.

The material balance for H_2, O_2, C was made for each run; and the minimum, maximum, absolute average deviation and standard deviation for all runs are shown in Table (1-A). On discussion of experimental results, the following remarks are presented in this chapter:

Water formation decreases when the percentage of O_2 in the feed decreases as shown in Figures 10, 11, and 12. The amount

of water formed increases as the contact time increases. This is particularly true at the lower O_2 percentages. Figures 5, 7, 8, 9, and 10 show that water production is not very sensitive to increased temperature. At 20% O_2 in the feed, the moles of water formed per mole of isobutane remained at about 0.095, for a contact time of 8 seconds, when the temperature was 350, 375, and 400°C.

The carbon monoxide and carbon dioxide formation is of particular interest. At 350°C. more CO than CO_2 is formed (Figures 10, 11, and 12). This ratio changes with temperature as shown in Figures 7, 9, and 10. Comparison of Figures 8 and 12 shows that CO production decreases with increased temperature for 40% O_2 in the feed. On the other hand, CO_2 production increases with increased temperature. At 350°C. more CO than CO_2 is formed for contact times greater than 7 seconds, while at 400°C. the reverse is true. This may be due to the water gas reaction:

$$H_2O + CO \text{-------} H_2 + CO_2$$

From Figures 7, 9, and 10 we see that the amount of formaldehyde and methanol produced is fairly independent of the related temperature and shows a slight increase with increased contact time.

Isobutylene and propylene production is always in the order of 3 to 6% as shown in Figures 5, 7, and 8. On the other hand, methane production is not greatly affected by per cent O_2 as can be seen in Figures 7 and 8.

Table 1*

A Sample Calculation

Run No. 46

Reactor Temperature = 375°C.

Reactor Pressure = 29.1 inches of Hg.

Components	%	Feed cc/hr	gr.mol/ hr	Gases Leaving Cold Trap mole fractions	gr.mole /hr.	Liquid Products From Cold Trap overall wt. %	gr. moles/ hr	Gases Leaving Reactor gr.mole /hr	mole fraction
H_2				.00029	.00019			.00019	.00024
O_2	39.3	7380	0.287	.23700	.15852			.15852	.19663
N_2			0.0027	.01566	.01047			.01047	.01299
CH_4				.00614	.00410			.00411	.00511
CO				.05040	.03371			.03371	.04181
CO_2				.05340	.03572			.03572	.04431
C_2H_6				.00007	.00005			.00005	.00006
C_2H_4				.00159	.00106			.00106	.00132
C_3H_8			0.003	.00650	.00435			.00435	.00540
C_3H_6				.01840	.01230			.01230	.01526

(Cont.)

Table 1 (Continued)

Components	%	Feed cc/hr	Feed gr.mol/hr	Gases Leaving Cold Trap mole fraction	Gases Leaving Cold Trap gr.mol/hr	Liquid Products From Cold Trap overall	Liquid Products From Cold Trap gr.mol/hr	Gases Leaving Reactor gr.mol/hr	Gases Leaving Reactor mole fraction
iC_4H_{10}	60.7	11400	0.43229	.56455	.37760			.37760	.46838
n C_4H_{10}			0.01212	.01340	.00896			.00896	.01111
iC_4H_8				.03260	.02180			.02180	.02704
Formaldehyde						16.21	.0151	.01510	.01871
Acetaldehyde						.415	.00026	.00026	.00032
Acetone						1.512	.00073	.00073	.00091
Methanol						4.971	.00434	.00434	.00538
H_2O						74.572	.11582	.11582	.14366
Acetic Acid						2.32	.00108	.00108	.00134

*where:

Feed temperature before heater = 84°F.

Feed pressure = 29.12 inches of Hg.

The temperature of gases leaving soapmeter = 84°F.

The pressure of gases leaving soapmeter = 29.08 inches of Hg.

Total liquid collected in cold trap = 2.7957 grams/hr.

Ideal gas law was assumed.

(Cont.)

Table 1 (Continued)

Material Balance:

Substance	gr.moles/hr In	gr.moles/hr Out	Difference	%Error
H_2	2.23441	2.22945	+0.00496	+0.22
O_2	.28700	.2803	+0.00670	+2.33
C	1.70691	1.78346	+0.00345	+0.19

Table (1-A)

Deviations	H_2	O_2	C
Absolute Average Differences %	0.350	1.46	0.30
Average Differences %	+ .005	+1.34	+ .06
Standard Deviation %	± .470	±1.28	±0.40
Maximum Deviation %	+1.040	+3.92	+1.11
Minimum Deviation %	-1.150	- .94	-1.04

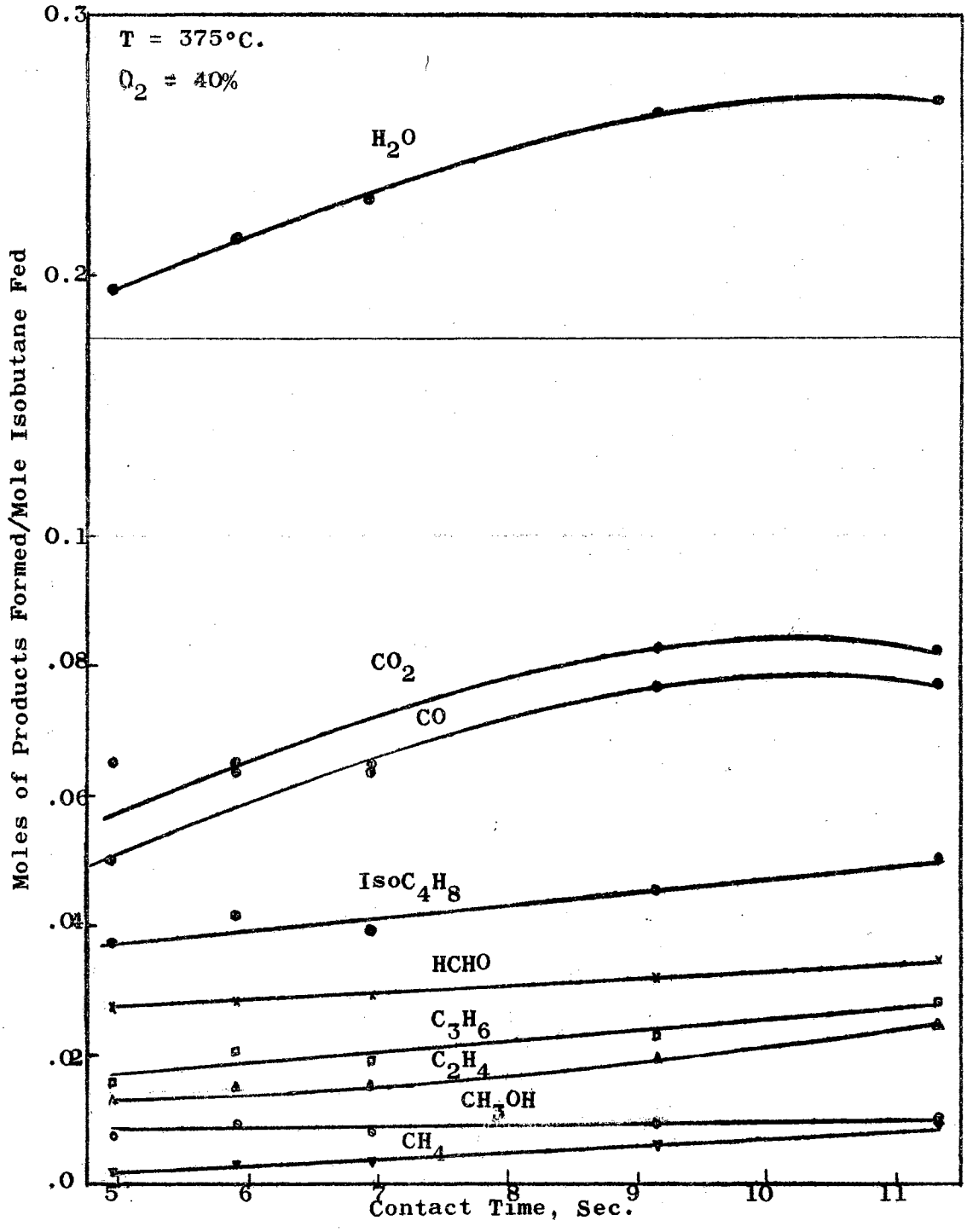

Figure 5

Product Distribution Curves at 375°C., 40% O_2

CHAPTER V

THE REACTION MECHANISM AND RATE EQUATION OF ISOBUTANE OXIDATION

The reaction mechanism of isobutane oxidation -

The partial oxidation of hydrocarbons can be explained by the concept of degenerate, or delayed, chain branching proposed by Semenov (25). According to this scheme, an intermediate builds up by the way of a primary chain reaction and can disappear by two simultaneous processes, one leading to new chain centers and the other to inert products. The mechanism of oxidation can best be described by the following three steps:

1- Initiation and delayed branching.

2- Propagation leading to formation of products and new chain centers.

3- Termination.

The partial oxidation of isobutane, similar to other hydrocarbons, follows the above mentioned three steps and proceeds through active centers in a branching - chain mechanism.

1- The initiation and delayed branching -

It is unlikely that the initial formation of active centers, atoms or radicals, is due to thermal cracking of isobutane because the temperature range used is below that required for onset of thermal decomposition. However, it has been shown that traces of oxygen will facilitate the pyrolysis of hydrocarbons (1).

In a straight chain hydrocarbon, the oxygen reacts with the second hydrogen from the end of the chain, while in a branched-chain hydrocarbon the oxygen will initially remove a tertiary hydrogen if one is available. An initiation step for the homogeneous n-butane oxidation, proposed by Skrivan and Hoelscher, involves activated oxygen molecules resulting from oxygen-oxygen collisions (26). A rate equation involving a second order oxygen dependence was derived and confirmed by testing against experimental data.

The tertiary C-H bond in isobutane is very reactive and it is unlikely that the reacting oxygen will need a very large amount of activation energy. Thus oxygen activation is not expected to be important in isobutane oxidation. It is likely that the initiation step for oxidation is the direct collision of isobutane-oxygen molecules. Isobutane is an exceptional hydrocarbon, in that it possesses nine primary and only one tertiary hydrogen. Therefore, the weak tertiary C-H bond is the most likely point for oxygen attack.

Egerton (8) has emphasized the combination of fuel molecule with oxygen as an essential step in combustion of hydrocarbons. Ubbelhode (34) describes a few advantages concerning the oxygen-hydrocarbon interaction as the initial step. According to Walsh (35), the point of oxygen attack in combustion of hydrocarbons is almost exclusively a tertiary C-H bond if present. Medley and Cooley (14) point out that the initial attack on the primary hydrogen atoms of isobutane is important at temperatures of 350°C. and above with pressure range of 100 to 2000 psig. Progressively more of the initial attack on isobutane occurs at the tertiary

hydrogen atom as the reaction temperature is lowered.

Thus the principal reactions of initiation step are:

(1) $isoC_4H_{10} + O_2 \text{-----} (CH_3)_3C^{\circ} + HO_2^{\circ}$

(2) $isoC_4H_{10} + O_2 \text{-----} (CH_3)_2CHCH_2^{\circ} + HO_2^{\circ}$

These reactions are endothermic to about 40 k cal/mole; and, therefore, the homogeneous reactions will be quite slow. The alkyl radicals thus formed react rapidly with oxygen and their reaction has an activation energy near zero (14, 31).

(3) $(CH_3)_3C^{\circ} + O_2 \text{-----} (CH_3)_3CO_2^{\circ}$

(4) $(CH_3)_2CHCH_2^{\circ} + O_2 \text{-----} (CH_3)_2CHCH_2O_2^{\circ}$

A third competitive reaction of the oxygen molecule with $isoC_4H_9^{\circ}$ radicals is the formation of isobutylene.

(5) $isoC_4H_9^{\circ} + O_2 \text{-----} isoC_4H_8 + HO_2^{\circ}$

This reaction becomes predominant as the temperature rises to the extent that reactions (2) and (3) become unimportant at high temperatures (1). The experimental data of Appleby (1) on n-butane oxidation shows the same trend. At the temperature range of this work, the fate of the $isoC_4H_9\ O_2^{\circ}$ radical is decomposition rather than absorption of hydrogen atom from hydrocarbon molecule (12,13). Thus, degenerate branching is brought about by decomposition of $isoC_4H_9\ O_2^{\circ}$ radical to formaldehyde, acetaldehyde, acetone and new chain centers.

(6) $(CH_3)_3CO_2^{\circ}$-----$(CH_3)_2CO + CH_3O^{\circ}$

(7a) $(CH_3)_2CHCH_2O_2^{\circ}$-----$(CH_3)_2CHO^{\circ} + HCHO$

(7b) $(CH_3)_2CHO^{\circ}$-----$CH_3CHO + CH_3^{\circ}$

2- Propagation -

The formation of products proceeds through decomposition of $isoC_4H_9\ O_2^{\circ}$ and $isoC_4H_9^{\circ}$ radicals to products and chain centers which, in turn, react with isobutane to produce new products and chain centers. The following approach explains some of the principal features leading to the formation of isobutane oxidation products. The products of isobutane oxidation are basically oxygenated compounds and unsaturated hydrocarbons. The oxygenated compounds are formed through the $isoC_4H_9\ O_2^{\circ}$ radical while the $isoC_4H_9^{\circ}$ radical gives rise to formation of unsaturated hydrocarbons.

Formaldehyde

Following reactions lead to the formation of formaldehyde which is present to considerable amount in reaction products of isobutane oxidation:

(7a) $(CH_3)_2CHCH_2O_2^{\circ}$-----$(CH_3)_2CHO^{\circ} + HCHO$

(8) $CH_3^{\circ} + O_2$-----$HCHO + OH^{\circ}$

Reaction (8) is exothermic with an activation energy between 1-3 k cal/mole (24). There is some question about the exact mechanism of reaction (8) as no spectroscopic OH bonds have been noted in

oxidation studies of methyl radical (24). A competing reaction with (8) is reaction (33) which will be discussed later on.

(33) $CH_3^o + isoC_4H_{10}$-----$CH_4 + isoC_4H_9^o$

Experimental data on isobutane oxidation , as indicated in Figures (7) and (8), show that the methane yield increases somewhat as the concentration of O_2 increases. This indicates that reaction (33) is predominant over reaction (8). Formaldehyde may decompose primarily by a free radical reaction of the form

(8a) $HCHO + isoC_4H_9^o$-----$CHO^o + isoC_4H_{10}$

leading to a new chain center.

Acetaldehyde

Acetaldehyde is formed through reaction (7b)

(7b) $(CH_3)_2CHO$-----$CH_3CHO + CH_3^o$

Acetaldehyde is found to a small amount in the products. Perhaps, this is partly due to the fact that reaction (1), the tertiary C-H bond attack by oxygen, is predominant over reaction (2). Besides, acetaldehyde is not a stable intermediate; it may react with free radicals.

(9) $CH_3CHO + isoC_4H_9^o$-----$isoC_4H_{10} + CH_3CO^o$

The acetyl radical is unstable (28) and readily decomposes to

(10) CH_3CO^o-----$CH_3^o + CO$

A second competitive reaction with (10) is oxidation of the

acetyl radical

(11) $CH_3CO^o + O_2 \text{-----} CO_2 + CH_3O^o$

(12) $CH_3CO^o + O_2 \text{-----} CH_3CO_3^o$

(13) $CH_3CO_3^o + isoC_4H_{10} \text{-----} isoC_4H_9^o + CH_3CO_3H$

(14) $CH_3CO_3H + CH_3CHO \text{-----} 2CH_3COOH$

leading to formation of acetic acid and CO_2.

Acetone

Acetone results through tertiary oxygen attack on isobutane. Reaction (7a) leads to the formation of acetone

(7a) $(CH_3)_3CO_2^o \text{-----} (CH_3)_2CO + CH_3O^o$

Methanol

The CH_3O^o radicals are responsible for formation of methanol (24).

(15) $CH_3O^o + isoC_4H_{10} \text{-----} CH_3OH + isoC_4H_9^o$

A competing reaction is the oxidation of CH_3O^o radical

(16) $CH_3O^o + O_2 \text{-----} CO + H_2O + OH^o$

Reaction (16) requires a decrease in methanol formation with an increase in oxygen concentration while our experimental data, Figures (7) and (8), show the reverse. Hence, reaction (15) is predominant over (16).

Water formation

HO_2^o and OH^o radicals available in the gas phase react with other molecules and radicals, dissociate or decompose on the wall. Basic reactions leading to formation of water are (6,13):

(17) $HO_2^o + isoC_4H_{10} \text{-----} H_2O_2 + isoC_4H_9^o$

(18) $HO_2^o + H_2 \text{-----} H_2O + OH^o$

(19) $HO_2^o + H_2 \text{-----} H_2O_2 + H^o$

(20) $2H\ O_2^o \xrightarrow{wall} H_2O_2 + O_2$

(21) $H_2O_2 \xrightarrow{dissociation} 2OH^o$

(22) $H_2O_2 + H^o + O_2 \text{-----} H_2O + O_2 + OH^o$

(23) $H_2O_2 \xrightarrow{decomposition\ on\ wall} H_2O + \frac{1}{2}O_2$

(24) $OH^o + isoC_4H_{10} \text{-----} H_2O + isoC_4H_9^o$

(25) $OH^o + H_2 \text{-----} H_2O + H^o$

Reaction (22) is a three body collision and has a low probability of occuring. The decomposition of HO_2^o and H_2O_2 on the wall is believed to occur less frequently, especially at the temperature and pressure of this work. These radicals and molecules encounter many collisions before arriving at the wall. Reaction

(18) is 62 k cal more exothermic than reaction (19) and has frequently been assumed to be the more probable reaction (6).

Thus the following reactions are believed to be responsible for formation of water:

(17) $HO_2^o + isoC_4H_{10} \text{-----} H_2O_2 + isoC_4H_9^o$

(18) $HO_2^o + H_2 \text{-----} H_2O + OH^o$

(21) $H_2O_2 \text{-----} 2OH^o$

(24) $OH^o + isoC_4H_{10} \text{-----} H_2O + isoC_4H_9^o$

(25) $OH^o + H_2 \text{-----} H_2O + H^o$

CO and CO_2

According to a scheme proposed by Tipper and Skirrow (32), with most fuels CO and CO_2 are produced solely from aldehydes

$$RCHO \xrightarrow{-H} RCO \begin{cases} \xrightarrow{} R + CO \\ \xrightarrow{O_2} CO_2 + \text{Products} \end{cases}$$

That is, CO and CO_2 do not come directly from reactions of radical R with oxygen but from intermediate aldehydes.

(9) $CH_3CHO + isoC_4H_9^o \text{-----} CH_3CO^o + isoC_4H_{10}$

(10) $CH_3CO^o \text{-----} CH_3^o + CO$

(26) $CH_3CO^o + O_2 \text{-----} CO_2 + CH_3O^o$

According to Dixon (7), the CO and oxygen reaction takes place much more readily in the presence of moisture than in the absence. He explained this by showing that the series of reactions

(27) $CO + H_2O \text{-----} CO_2 + H_2$

(28) $2H_2 + O_2 \text{-----} 2H_2O$

take place more readily than the direct oxidation. The experimental data on isobutane oxidation show that at 350°C. more CO is formed than CO_2, but at 375°C. and 400°C. the reverse is true. This may be due to the above water gas reaction.

(27) $CO + H_2O \text{-----} CO_2 + H_2$

Besides, an increase in H_2 formation with increase in temperature, as observed experimentally, favors this reaction.

Formation of H_2, CH_4, C_2H_4, C_2H_6, C_3H_6, $isoC_4H_8$-

The following reactions are considered to be responsible for the formation of the above products (1,13).

(8a) $HCHO + isoC_4H_9^o \text{-----} CHO^o + isoC_4H_{10}$

(29) $CHO^o \text{-----} CO + H^o$

(30) $H^o + isoC_4H_{10} \text{-----} H_2 + isoC_4H_9^o$

(31) $isoC_4H_9^o \text{-----} CH_3^o + C_3H_6$

(32) $isoC_4H_9^o \text{-----} C_2H_5^o + C_2H_4$

(33) $CH_3^o + isoC_4H_{10} \text{-----} CH_4 + isoC_4H_9^o$

(34) $C_2H_5^o + isoC_4H_{10} \text{-----} C_2H_6 + isoC_4H_9^o$

(35) $C_2H_5^o \text{-----} C_2H_4 + H^o$

(5) $isoC_4H_9^o + O_2 \text{-----} isoC_4H_8 + HO_2^o$

3- Termination

Chain centers present in the vapor phase oxidation of isobutane finally combine and terminate further chain reactions. Termination can occur homogeneously by free radical recombination or disproportion reactions. Because of the retarding effect of the surface of reaction vessel on the rate of reaction, many investigators have suggested that chain termination occurs by destruction of radicals on the vessel walls. Several different radicals are present in the gas-phase oxidation, and so the choice of termination steps is difficult and in many cases, to some extent, a matter of personal preference. At the temperature and pressure of isobutane oxidation, free radicals will encounter many collisions before arriving at the wall. Hence, the termination steps are considered to take place in vapor phase.

Hinshelwood and his co-workers (10) have explained the kinetics of slow combustion of n-butane, n-hexane, and butanone on the assumption that a termination step is

$$R^o + O_2 \text{-----} \text{inert products}$$

Considering the termination step in isobutane oxidation a reaction similar to the above reaction we have

$isoC_4H_9^o + O_2$-----inert products

From what is described earlier, the following reaction mechanism is suggested to represent the mode of partial oxidation of isobutane.

THE SCHEME OF ISOBUTANE OXIDATION REACTIONS

(1) $isoC_4H_{10} + O_2$-----$(CH_3)_3C^o + HO_2^o$

(2) $isoC_4H_{10} + O_2$-----$(CH_3)_2CHCH_2^o + HO_2^o$

(3) $(CH_3)_3C^o + O_2$-----$(CH_3)_3CO_2^o$

(4) $(CH_3)_2CHCH_2^o + O_2$-----$(CH_3)_2CHCH_2O_2^o$

(5) $isoC_4H_9^o + O_2$-----$isoC_4H_8 + HO_2^o$

(6) $(CH_3)_3CO_2^o$-----$(CH_3)_2CO + CH_3O^o$

(7) $(CH_3)_2CHCH_2O_2^o$-----$(CH_3)_2CHO^o + HCHO$

(8) $(CH_3)_2CHO^o$----$CH_3CHO + CH_3^o$

(9) $CH_3CHO + isoC_4H_9^o$-----$CH_3CO^o + isoC_4H_{10}$

(10) CH_3CO^o-----$CO + CH_3^o$

(11) $CH_3CO^o + O_2$-----$CO_2 + CH_3O^o$

(12) $CO + H_2O \text{-----} CO_2 + H_2$

(13) $CH_3O^o + isoC_4H_{10} \text{-----} CH_3OH + isoC_4H_9^o$

(14) $HCHO + isoC_4H_9^o \text{-----} isoC_4H_{10} + CHO^o$

(15) $CHO^o \text{-----} CO + H^o$

(16) $H^o + isoC_4H_{10} \text{-----} H_2 + isoC_4H_9^o$

(17) $isoC_4H_9^o \text{-----} C_3H_6 + CH_3^o$

(18) $CH_3^o + isoC_4H_{10} \text{-----} CH_4 + isoC_4H_9^o$

(19) $isoC_4H_9^o \text{-----} C_2H_4 + C_2H_5^o$

(20) $C_2H_5^o + isoC_4H_{10} \text{-----} C_2H_6 + isoC_4H_9^o$

(21) $C_2H_5^o \text{-----} C_2H_4 + H^o$

(22) $HO_2^o + isoC_4H_{10} \text{-----} H_2O_2 + isoC_4H_9^o$

(23) $HO_2^o + H_2 \text{-----} H_2O + OH^o$

(24) $H_2O_2 \text{-----} 2OH^o$

(25) $OH^o + isoC_4H_{10} \text{-----} H_2O + isoC_4H_9^o$

(26) $isoC_4H_9^o + O_2$-----inert products

Reaction Rate Equation -

Based on the reaction scheme proposed for partial oxidation of isobutane and the assumption made that the oxygen reactions are irreversible, the overall rate of oxygen reactions becomes:

(a) $$\frac{-d(O_2)}{dt} = (k_1+k_2)(O_2)(isoC_4H_{10}) + (k_3+k_4+k_5+k_{26})(isoC_4H_9^o)(O_2) + k_{11}(CH_3CO^o)(O_2)$$

Assuming steady-state conditions prevail, we have:

(b) $$\frac{-d(isoC_4H_9^o)}{dt} = (k_3+k_4+k_5)(isoC_4H_9^o)(O_2) - (k_1+k_2)(isoC_4H_{10})(O_2) + k_9(isoC_4H_9^o)(CH_3CHO) - k_{13}(CH_3O^o)(isoC_4H_{10}) + k_{14}(HCHO)(isoC_4H_9^o) - k16(H^o)(isoC_4H_{10}) + k_{17}(isoC_4H_9^o) - k_{18}(CH_3^o)(isoC_4H_{10}) + k_{19}(isoC_4H_9^o) - k_{20}(C_2H_5^o)(isoC_4H_{10}) - k_{25}(OH^o)(isoC_4H_{10}) + k_{26}(isoC_4H_9^o)(O_2) = 0$$

(c) $$\frac{-d(CHO^o)}{dt} = - k_{14}(HCHO)(isoC_4H_9^o) + k_{15}(CHO^o) = 0$$

(d) $$\frac{-d(H^o)}{dt} = - k_{15}(CHO^o) + k_{16}(H^o)(isoC_4H_{10}) + k_{21}(C_2H_5^o) = 0$$

(e) $$\frac{-d(OH^o)}{dt} = - k_{23}(HO_2^o)(H_2) - k_{24}(H_2O_2) + k_{25}(OH^o)(isoC_4H_{10})=0$$

(f) $$\frac{-d(CH_3^o)}{dt} = -k_8[(CH_3)_2CHO^o] - k_{10}(CH_3CO^o) - k_{17}(isoC_4H_9^o) + k_{18}(CH_3^o)(isoC_4H_{10}) = 0$$

(g) $$\frac{-d(C_2H_5^o)}{dt} = -k_{19}(isoC_4H_9^o) + k_{20}(isoC_4H_{10})(C_2H_5^o) + k_{21}(C_2H_5^o) = 0$$

(h) $$\frac{-d(CH_3CO^o)}{dt} = -k_9(CH_3CHO)(isoC_4H_9^o) + k_{10}(CH_3CO^o) + k_{11}(CH_3CO^o)(O_2) = 0$$

(i) $$\frac{-d(HO_2^o)}{dt} = -(k_1+k_2)(isoC_4H_{10})(O_2) - k_5(isoC_4H_9^o)(O_2) + k_{22}(HO_2^o)(isoC_4H_{10}) + k_{23}(HO_2^o)(H_2) = 0$$

(j) $$\frac{-d(CH_3O^o)}{dt} = -k_{11}(CH_3CO^o)(O_2) + k_{13}(CH_3O^o)(isoC_4H_{10}) - k_6[(CH_3)_3CO_2^o] = 0$$

(k) $$\frac{-d(H_2O_2)}{dt} = -k_{22}(HO_2^o)(isoC_4H_{10}) + k_{24}(H_2O_2) = 0$$

(m) $$\frac{-d[(CH_3)_3CO_2^o]}{dt} = -k_3(isoC_4H_9^o)(O_2) + k_6[(CH_3)_3CO_2^o] = 0$$

From the above equations:

From (c)

$$k_{14}(HCHO)(isoC_4H_9^o) = k_{15}(CHO^o)$$

From (d) and (c)

(1) $k_{14}(HCHO)(isoC_4H_9^o) = k_{15}(CHO^o) = - k_{21}(C_2H_5^o)+k_{16}(H^o)(isoC_4H_{10})$

From (j) and (m)

(2) $k_{11}(CH_3CO^o)(O_2) = k_{13}(CH_3O^o)(isoC_4H_{10}) - k_3(isoC_4H_9^o)(O_2)$

From (h)

(3) $k_9(CH_3CHO)(isoC_4H_9^o) = k_{10}(CH_3CO^o) + k_{11}(C\ H_3CO^o)(O_2)$

From (f)

(4) $k_{10}(CH_3CO^o) = - k_8[(CH_3)_2CHO] - k_{17}(isoC_4H_9^o)+k_{18}(CH_3^o)(isoC_4H_{10})$

From (2), (3), (4)

(5) $k_9(CH_3CHO)(isoC_4H_9^o) = -k_8[(CH_3)_2CHO] - k_{17}(isoC_4H_9^o) + k_{18}$

$(CH_3^o)(isoC_4H_{10}) + k_{13}(CH_3O^o)(isoC_4H_{10}) - k_3(isoC_4H_9^o)(O_2)$

From (g)

$-k_{21}(C_2H_5^o) = -k_{19}(isoC_4H_9^o) + k_{20}(isoC_4H_{10})(C_2H_5^o)$

From (g) and (m)

(6) $k_{14}(HCHO)(isoC_4H_9^o) = k_{16}(H^o)(isoC_4H_{10}) - k_{19}(isoC_4H_9^o)$

$+ k_{20}(isoC_4H_{10})(C_2H_5^o)$

From (e), (i), (k)

(7) $-(k_1+k_2)(isoC_4H_{10})(O_2) - k_5(isoC_4H_9^o)(O_2) = -k_{25}(OH^o)(isoC_4H_{10})$

But

$$\frac{-d[(CH_3)_2CHCH_2O_2^\circ]}{dt} = -k_4(isoC_4H_9^\circ)(O_2) + k_7[(CH_3)_2CHCH_2O_2^\circ] = 0$$

$$\frac{-d[(CH_3)_2CHO^\circ]}{dt} = -k_7[(CH_3)_2CHCH_2O_2^\circ] + k_8[(CH_3)_2CHO^\circ] = 0$$

Hence

$$(8)\quad -k_8[(CH_3)_2CHO] = -k_4(isoC_4H_9^\circ)(O_2)$$

From (b), (5), (6), (7), (8)

$$(9)\quad (isoC_4H_9^\circ)(O_2) = \left(\frac{2(k_1+k_2)}{k_{26}+k_4 - k_4}\right)(isoC_4H_{10})(O_2)$$

$$(isoC_4H_9^\circ)(O_2) = K_1(isoC_4H_{10})(O_2)$$

Where

$$K_1 = \frac{2(k_1+k_2)}{k_{26}}$$

On the other hand

$$-k_9(CH_3CHO)(isoC_4H_9^\circ) + k_{10}(CH_3CO^\circ) + k_{11}(CH_3CO^\circ)(O_2) = 0$$

$$(CH_3CO^\circ)(O_2) = \frac{k_9(CH_3CHO)(isoC_4H_9^\circ)(O_2)}{k_{10}+k_{11}(O_2)}$$

$k_{10} > k_{11}(O_2)$, reaction (10) is much faster than (11)

$$k_{11}(CH_3CO^\circ)(O_2) = \frac{k_{11}k_9(CH_3CHO)(isoC_4H_9^\circ)(O_2)}{k_{10}}$$

But concentration of (CH_3CHO) is almost constant as seen from Table (2), thus we have,

$$k_{11}(CH_3CO^o)(O_2) = K_{11}(isoC_4H_9^o)(O_2) = K_{11}K_1(isoC_4H_{10})(O_2)$$

Where

$$K_{11} = \frac{k_{11}k_9(CH_3CHO)}{k_{10}}$$

Or

$$k_{11}(CH_3CO^o)(O_2) = K_2(isoC_4H_{10})(O_2)$$

Where

$$K_2 = K_{11}K_1$$

Hence

$$\frac{-d(O_2)}{dt} = (k_3+k_4+k_5+k_{26})K_1(isoC_4H_{10})(O_2) + K_3(isoC_4H_{10})(O_2)$$

where $K_3 = k_1 + k_2 + K_2$

Or

$$\frac{-d(O_2)}{dt} = \left[K_1(k_3+k_4+k_5+k_{26})+K_3\right](isoC_4H_{10})(O_2)$$

Therefore

$$\frac{-d(O_2)}{dt} = k(isoC_4H_{10})(O_2) \quad (10)$$

Where k, the reaction rate constant, $k = K_1(k_3+k_4+k_5+k_{26})+K_2$

If we consider reaction 12 is predominant over 11, then in the rate equation the term $k_{11}(CH_3CO^o)(O_2)$ will drop out and

previous discussion will lead again to the same conclusion that the rate of oxygen consumption has a second order dependence on oxygen-isobutane concentrations with equal power.

The overall rate of reaction proposed by Appleby (1) and Skrivan (26) for n-butane oxidation has the form of

$$\text{Appleby:} \quad r = \frac{-d(n\text{-}C_4H_{10})}{dt} = kC_{O_2}^{1/2} C_{n\text{-}C_4}^{3/2}$$

$$\text{Skrivan:} \quad r = \frac{-d(n\text{-}C_4H_{10})}{dt} = kC_{O_2}^{2}$$

The overall maximum rate equation proposed by Hinshelwood and co-workers for n-Pentane, n-hexane, and butanone has the form of (11)

$$r_{max.} = \frac{-d(O_2)}{dt} = \frac{C_1(RH)(O_2)}{1 - \frac{C_2(RH)}{(O_2)+C_3(RH)}}$$

Where C_1, C_2, C_3 are constants.

Taking into consideration that C_3 is about 20.5 in n-Pentane oxidation and $(RH) > (O_2)$, one can neglect the term (O_2) in the denominator leading to

$$r_{max.} = k(RH)(O_2)$$

The overall rate of oxygen consumption in isobutane oxidation, based on reaction scheme suggested, has the form of

$$r = \frac{-d(O_2)}{dt} = \frac{dX}{dt} = k(C_{O_2})(C_{isoC_4H_{10}})$$

Where:

r = rate of reaction, sec.$^{-1}$

X = moles O_2 converted/mole fed

t = time in seconds

k = reaction rate constant, sec.$^{-1}$

C_{O_2} = O_2 mole fraction in exit from reactor

C_{isoC4} = isobutane mole fraction in exit from reactor

Considering the following nomenclature for integration of the above equation:

N_i^o = moles of i fed to the reactor/hr.

N_i = moles of i component leaving the reactor/hr.

E = total moles/hr of gases leaving reactor

$$q = \frac{\text{moles of isobutane converted/mole fed}}{\text{moles } O_2 \text{converted/mole fed}}$$

Y = moles of isobutane converted/mole fed

$M = N^o_{isoC_4}/N^o_{O_2}$

Hence we have:

$$(C_{O_2}) = (1-X)\frac{N^o_{O_2}}{E}$$

$$Y = qX$$

$$(isoC_4) = \frac{N_{isoC4}}{E} = \frac{N^o_{isoC4}\ (1-qX)}{E}$$

$$(isoC_4) = (1-qX)\frac{N^o_{isoC_4}}{E}$$

but

$$N^o_{isoC_4} = M\ N^o_{O_2}$$

Hence:

$$(isoC_4) = (1-qX)\ \frac{M}{E}\ N^o_{O_2}$$

Inserting values of isobutane and O_2 mole fractions in rate equation:

$$r = \frac{dX}{dt} = k\left[(1-X)\ \frac{N^o_{O_2}}{E}\right]\left[(1-qX)\left(\frac{MN^o_{O_2}}{E}\right)\right]$$

upon integration and assumption that q is constant

$$\int \frac{dX}{(1-X)(1-qX)} = \int k\left[\left(\frac{N^o_{O_2}}{E}\right)^2 M\right]\ dt$$

or

$$\ln\left(\frac{1-qX}{1-X}\right) = k\ (1-q)\left(\frac{N^o_{O_2}}{E}\right)^2 Mt$$

Taking

$$K = \left[(1-q)\ \left(\frac{N^o_{O_2}}{E}\right)^2\right]M$$

and

$$K' = kK$$

we have:

$$\ln\ \left(\frac{1-qX}{1-X}\right) = K't$$

In Tables (3) through (15) values of K have been evaluated for all experimental runs. The results show that K remains reasonably constant. Tables (3) through (15) are given in Appendix II.

In order to check the validity of the above reaction rate equation developed from the suggested scheme for partial oxidation of isobutane, plots of $\ln(1-qX)/(1-X)$ versus contact time should yield a straight line with slope equivalent to K'.

Figures (13) through (19) show that the reaction rate equation represents experimental data. The reaction rate constants thus obtained are shown in Table (17) of Appendix II for different temperatures.

Activation Energy -

The Arrhenius equation (27) gives the relationship between reaction rate constant and temperature:

$$k = Ae^{-E/RT}$$

where

k = Reaction rate constant

A = Frequency factor

E = Activation energy

R = Constant

T = Absolute temperature

According to this equation, a plot of ln(k) versus 1/T should yield a straight line with a slope of -E/R and an intercept of ln(A).

Figure (6) represents such a plot for oxygen concentrations of 20% and 40% O_2. The result shows an activation energy equivalent to 15.0, and 18.4 k cal/mole for 20% and 40% oxygen, respectively. The rate constant for 20% oxygen at 400°C., as shown in Table (17) is lower than expected. This is perhaps due to the fact that at the temperature range of 325-425°C. the

negative temperature coefficient should be expected, especially for hydrocarbon rich mixtures as described by Prettre(21) and Townend (33). According to Chung(5), one of the reasons for the negative temperature occurence is the competition between reactions (3) and (4) with (5) of the reaction scheme described earlier where reaction (5) is a non-branching reaction.

It is interesting to note that the activation energy calculated for two concentrations of oxygen are close and in agreement with that reported (16 k cal/mole) in the literature (4). But, it should be mentioned that the rate constants evaluated and shown in Table (17) are dependent on initial oxygen concentration. This is true for rate constants presented by Skrivan (26) and Appleby (1) on n-butane oxidation. However, it is possible, by introducing an approximate factor of $(C^{o}_{O_2})^{-1.5}$ in rate equation developed here and $(C^{o}_{O_2})^{-2.0}$ in Skrivan rate equation, to overcome this problem.

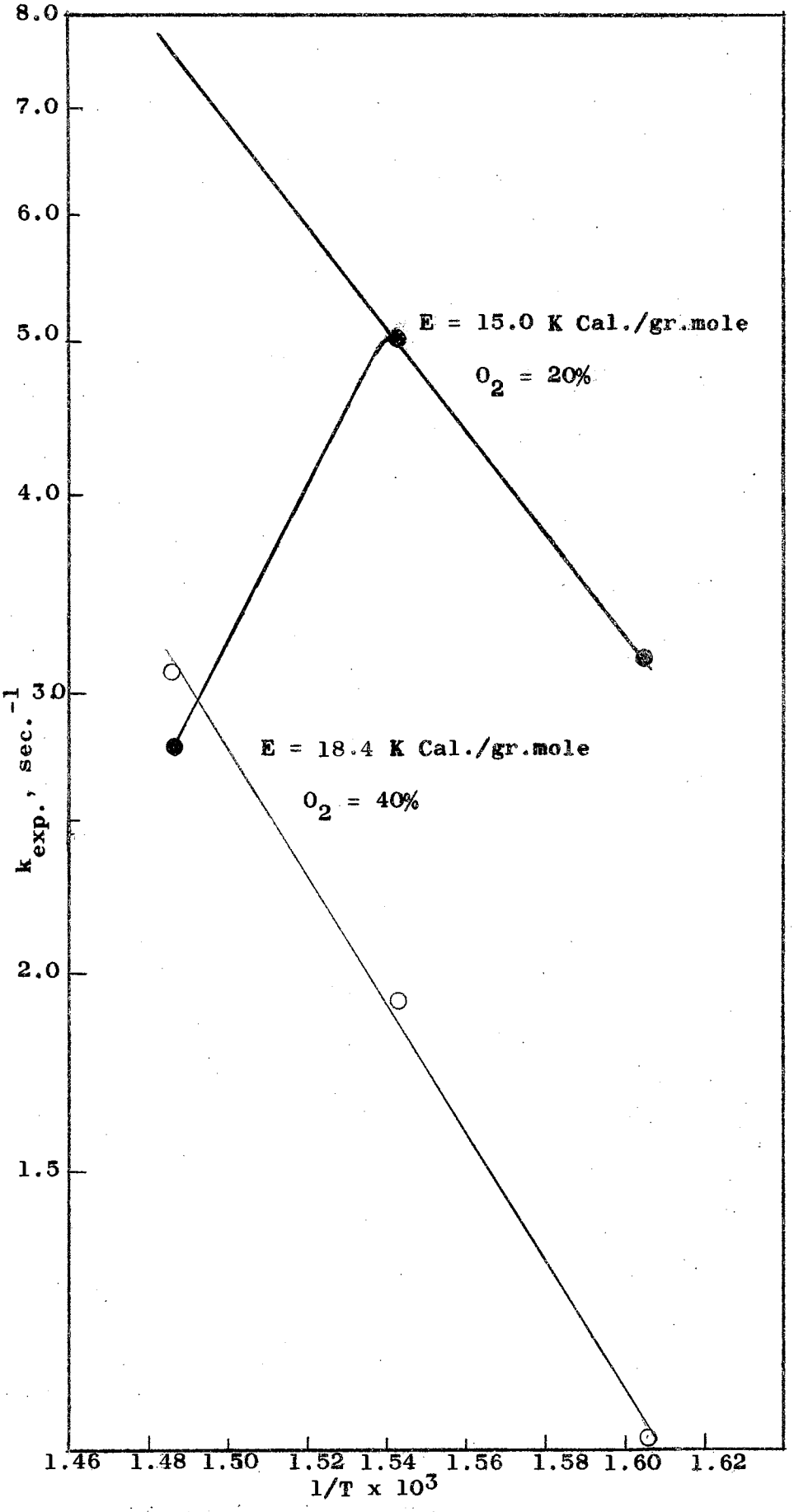

Figure 6 ln(k) versus $\frac{1}{T}$

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

The partial oxidation of isobutane has been investigated in the temperature range of 350-400°C. The results have been shown in terms of product distributions. A rate equation has been developed which fits the experimental data and explains the mode of reaction mechanism. The reaction mechanism of isobutane oxidation has been discussed in detail and a scheme of intermediate steps leading to products of the reaction has been suggested which is in accordance with experimental data.

The temperature range used is a transition region between low and high temperature oxidation of hydrocarbons. In this region cool flame phenomenon and negative temperatures should be expected. The data on reaction rate constants discussed in Chapter V explainsthe negative temperature coefficient phenomenon for isobutane rich feed (80%). The rate constant increases with temperature up to 375°C. and then drops as temperature approaches 400°C. Oxygen-rich feed does not show this abnormality. The activation energy evaluated is in agreement with the value found in the literature (4).

The writer believes that the partial oxidation of hydrocarbons is a vast area which deserves more research. The cool flame phenomenon and negative temperature coefficient phenomenon are important areas for more investigation. The effects of surface

and surface-to-volume-ratio of the reactor have not been well formulated; hence, they need more attention in future investigations.

The author hopes that future research in the area of partial oxidation will throw more light on the understanding of hydrocarbon oxidation mechanisms and the intermediate compound (s) responsible for degenerate branching.

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APPENDIX I

PRODUCT DISTRIBUTION

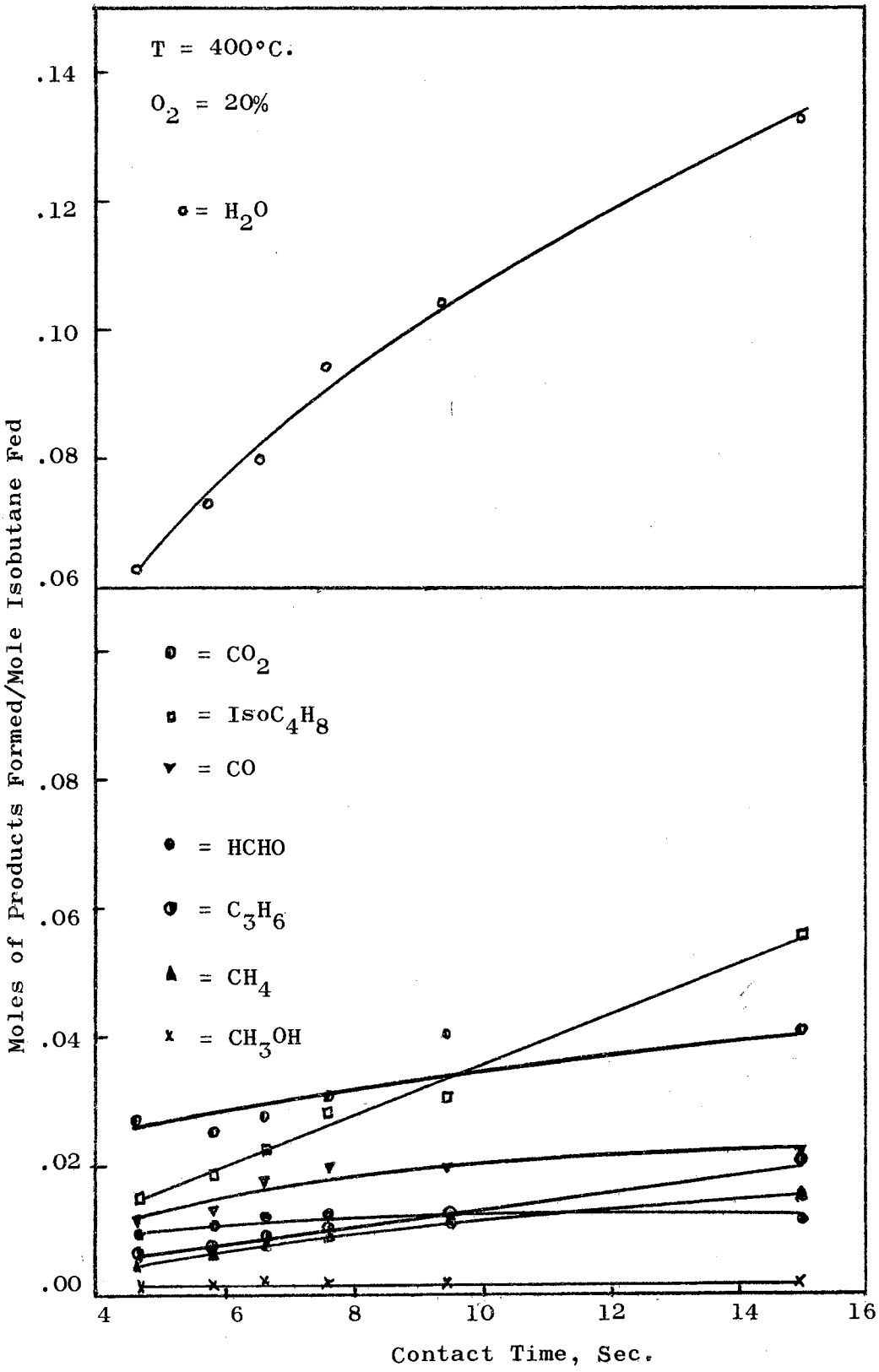
T = 400°C.
O_2 = 20%
o = H_2O
= CO_2
= $IsoC_4H_8$
= CO
= HCHO
= C_3H_6
= CH_4
= CH_3OH
.14
.12
.10
.08
.06
.08
.06
.04
.02
.00
4
6
8
10
12
14
16
Moles of Products Formed/Mole Isobutane Fed
Contact Time, Sec.

Figure 7

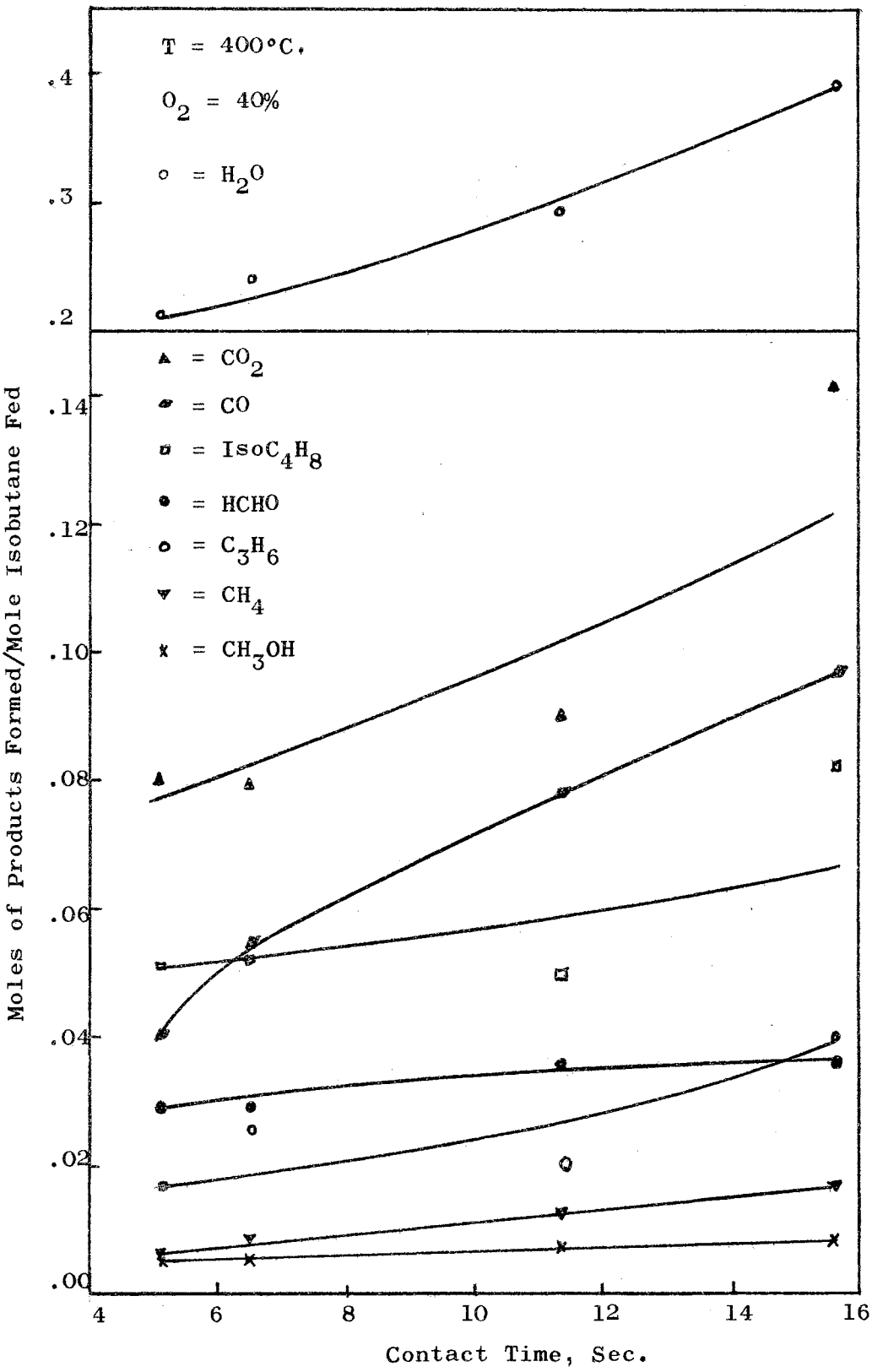
T = 400°C.
O_2 = 40%
o = H_2O
▲ = CO_2
= CO
= $IsoC_4H_8$
● = HCHO
o = C_3H_6
▼ = CH_4
x = CH_3OH
.4
.3
.2
.14
.12
.10
.08
.06
.04
.02
.00
4
6
8
10
12
14
16
Moles of Products Formed/Mole Isobutane Fed
Contact Time, Sec.

Figure 8

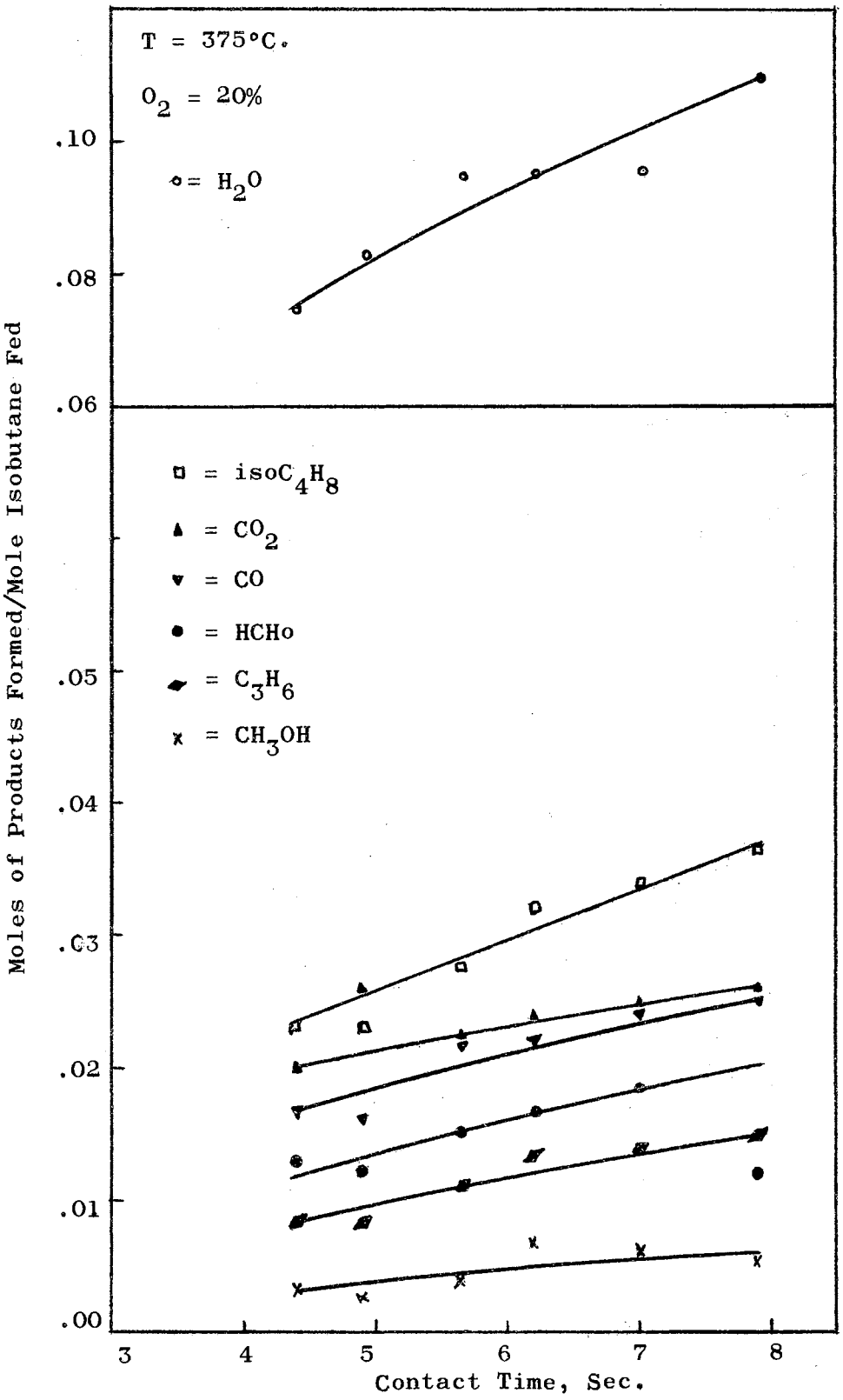
T = 375°C.
O_2 = 20%
o = H_2O
□ = $isoC_4H_8$
▲ = CO_2
▼ = CO
● = HCHo
◆ = C_3H_6
x = CH_3OH
Moles of Products Formed/Mole Isobutane Fed
.10
.08
.06
.05
.04
.03
.02
.01
.00
3
4
5
6
7
8
Contact Time, Sec.

Figure 9

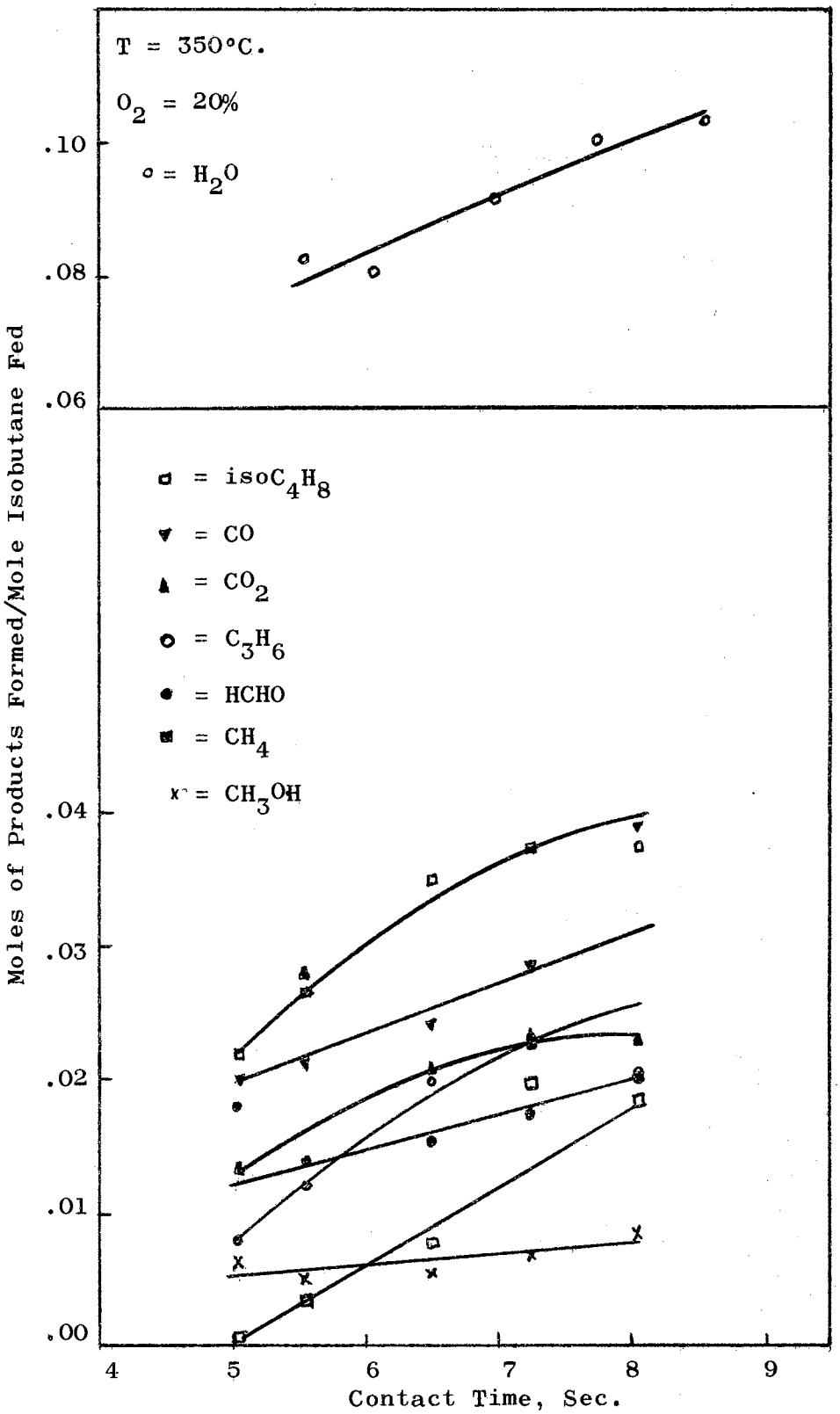
T = 350°C.
O_2 = 20%
o = H_2O
□ = $isoC_4H_8$
▼ = CO
▲ = CO_2
○ = C_3H_6
● = HCHO
■ = CH_4
x = CH_3OH
Moles of Products Formed/Mole Isobutane Fed
.10
.08
.06
.04
.03
.02
.01
.00
4
5
6
7
8
9
Contact Time, Sec.

Figure 10

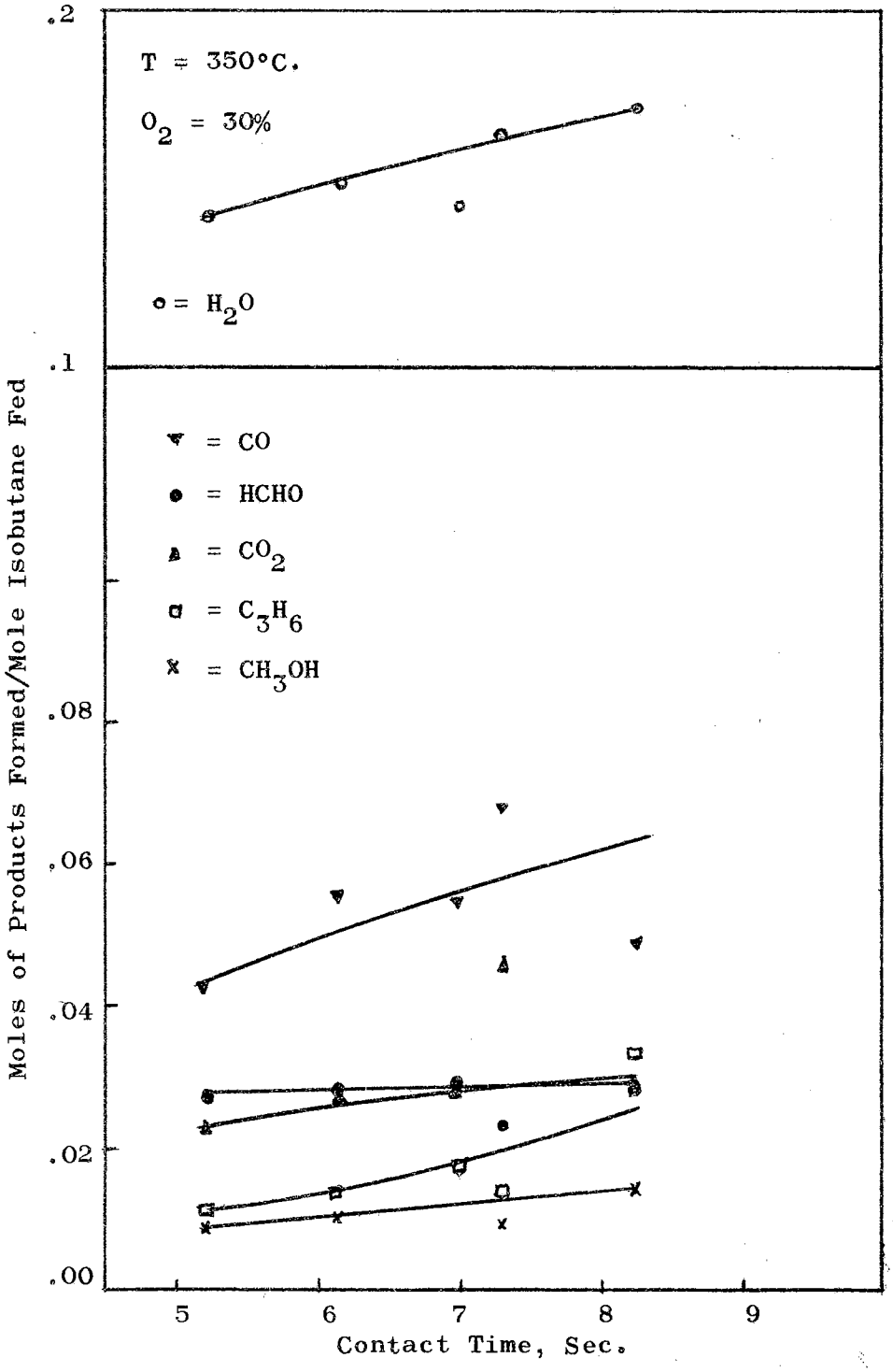
.2
T = 350°C.
O_2 = 30%
o = H_2O
.1
= CO
= HCHO
= CO_2
= C_3H_6
= CH_3OH
.08
.06
.04
.02
.00
Moles of Products Formed/Mole Isobutane Fed
5
6
7
8
9
Contact Time, Sec.

Figure 11

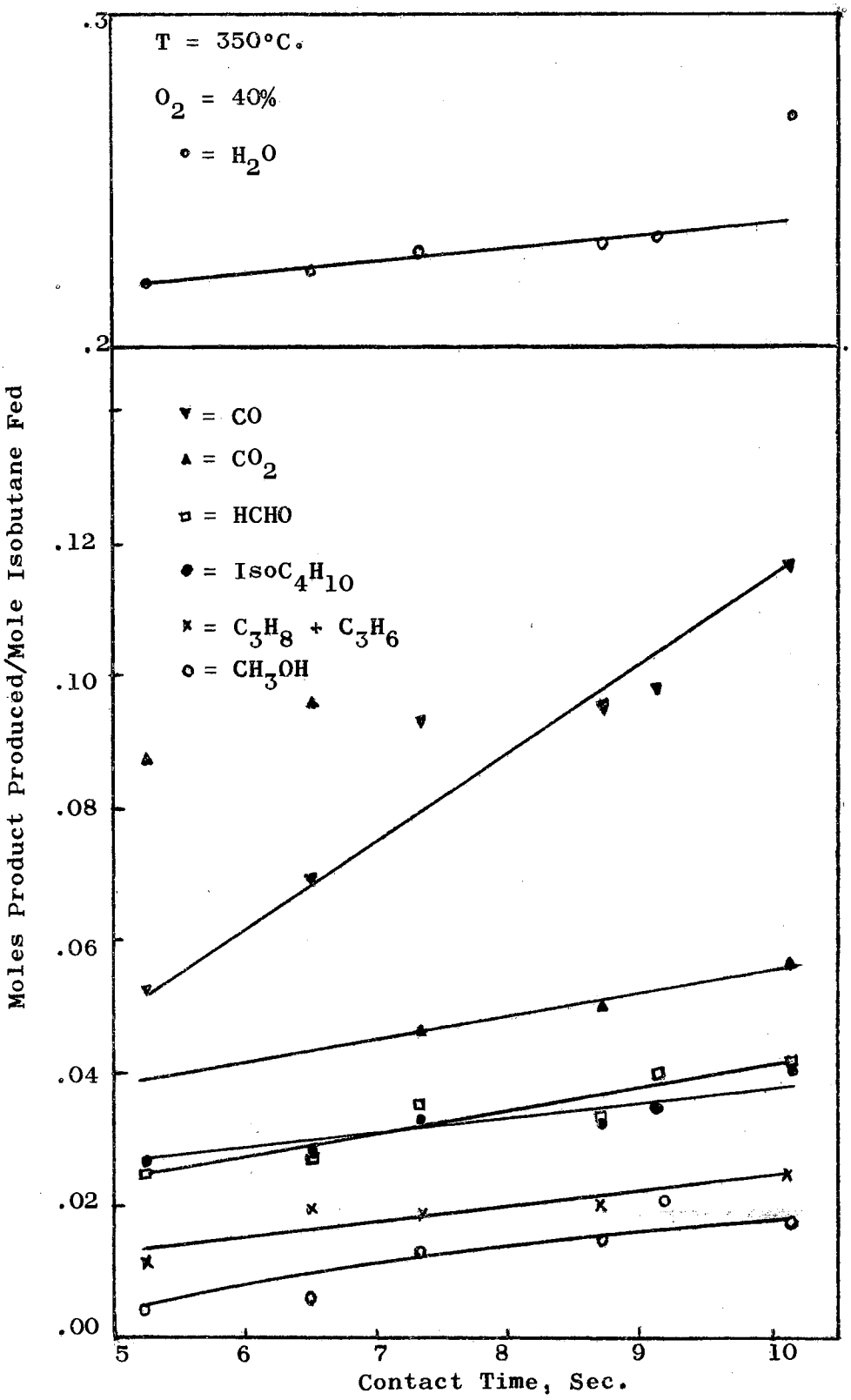
T = 350°C.
O_2 = 40%
= H_2O
= CO
= CO_2
= HCHO
= $IsoC_4H_{10}$
= C_3H_8 + C_3H_6
= CH_3OH
Moles Product Produced/Mole Isobutane Fed
.3
.2
.12
.10
.08
.06
.04
.02
.00
5
6
7
8
9
10
Contact Time, Sec.

Figure 12

Table (2)

Moles/hr. of Gases In and Out of Reactor

Run No.	19	20	21
Reactor Temperature, °C.	350	350	350
Reactor Pressure, in.	29.9	29.9	29.9
Temperature of gases leaving soapmeter, °F.	81	81	81
Pressure of gases leaving soapmeter, in.	29.17	29.17	29.17
Gr. moles/hr. O_2 fed to reactor**	.659	.55	.473
Gr. moles/hr. i-C_4H_{10} fed to reactor**	.959	.79792	.6884
Gases leaving reactor	Gr. moles/hr.		
H_2	.00181	.00033	.00005
O_2	.40921	.34036	.29133
N_2	.00794	.00649	.00932
CH_4	.00813	.00730	.00165
CO	.05028	.05505	.06431
CO_2	.08456	.07747	.03215
C_2H_6	-	-	-
C_2H_4	-	-	-
C_3H_8	.01140*	.01584*	.01282*
C_3H_6	-	-	-
i-C_4H_{10}	.87731	.71831	.62075
n-C_4H_{10}	.03322	.02592	.02395
i-C_4H_8	.02614	.02283	.02266
HCHO	.02411	.02207	.02453
CH_3CHO	.00025	.00030	.00043
CH_3COCH_3	.00052	.00076	.00153
CH_3OH	.00428	.00481	.00923
H_2O	.21003	.17749	.15698
CH_3COOH	.00180	.00160	.00244

* C_3H_8 + C_3H_6

** without impurities

Table (2) (Continued)

Run No.	22**	23	24
Reactor Temperature, °C.	350	350	350
Reactor Pressure, in.	29.9	29.7	29.9
Temperature of gases leaving soapmeter, °F.	81	76	81
Pressure of gases leaving soapmeter, in.	29.17	29.12	29.17
Gr. moles/hr. O_2 fed to reactor	.393	.3723	.331
Gr. moles/hr. i-C_4H_{10} fed to reactor	.51717	.5538	.481
Gases leaving reactor	Gr. moles/hr.		
H_2	.00005	.00020	.00011
O_2	.25714	.22519	.19224
N_2	.00793	.00469	.00262
CH_4	.00322	.00146	.00331
CO	.05474	.05460	.05647
CO_2	.02880	.02218	.02745
C_2H_6	-	.00002	-
C_2H_4	-	.00106	-
C_3H_8	.01150*	.00554	.01212*
C_3H_6	-	.01120	-
i-C_4H_{10}	.51842	.49620	.41649
n-C_4H_{10}	.02010	.01129	.01765
i-C_4H_8	.01830	.01935	.01955
HCHO	.01885	.02250	.02032
CH_3CHO	.00036	.00093	.00048
CH_3COCH_3	.00136	.00258	.00157
CH_3OH	.00881	.01183	.00857
H_2O	.13175	.12881	.12929
CH_3COOH	.00188	.00188	.00171

* C_3H_8 + C_3H_6

** Runs 22 and 25 were not considered in k calculations for uncertainly in gas phase.

Table (2) (Continued)

Run No.	25	26	27
Reactor Temperature, °C.	350	350	350
Reactor Pressure, in.	29.9	29.9	29.72
Temperature of gases leaving soapmeter, °F.	81	81	75
Pressure of gases leaving soapmeter, in.	29.17	29.17	29.12
Gr. moles/hr. O_2 fed to reactor	.486	.4158	.365
Gr. moles/hr. i-C_4H_{10} fed to reactor	1.1135	.9408	.84289
Gases leaving reactor	Gr. moles/hr.		
H_2	.00002	.00006	.00034
O_2	.32136	.26119	.23390
N_2	.01968	.00354	.00442
CH_4	.00154	.00160	.00152
CO	.04759	.05224	.04609
CO_2	.02550	.02651	.02385
C_2H_6	-	-	.00002
C_2H_4	-	-	.00088
C_3H_8	.01313*	.01280*	.00938
C_3H_6	-	-	.01524
i-C_4H_{10}	.96562	.86502	.77377
n-C_4H_{10}	.08907	.04312	.01904
i-C_4H_8	.06149	.02692	.02955
HCHO	.02991	.02570	.02473
CH_3CHO	.00032	.00042	.00092
CH_3COCH_3	.00212	.00120	.00174
CH_3OH	.00990	.00937	.01360
H_2O	.15816	.14674	.12202
CH_3COOH	.00246	.00224	.00189

* C_3H_8 + C_3H_6

Table (2) (Continued)

Run No.	28	29	30
Reactor Temperature, °C.	350	350	350
Reactor Pressure, in.	29.9	29.85	29.7
Temperature of gases leaving soapmeter, °F.	81	78	73
Pressure of gases leaving soapmeter, in.	29.17	29.35	29.12
Gr. moles/hr. O_2 fed to reactor	.3104	.3505	.3406
Gr. moles/hr. i-C_4H_{10} fed to reactor	.70225	.7942	1.33666
Gases leaving reactor	Gr. moles/hr.		
H_2	.00005	.00050	.00020
O_2	.18050	.21600	.23100
N_2	.00287	.00805	.00635
CH_4	.00248	.01627	.00109
CO	.04785	.03905	.02689
CO_2	.02072	.03707	.01815
C_2H_6	-	.00028	.00020
C_2H_4	-	.00154	.00040
C_3H_8	.00992*	.01151	.01336
C_3H_6	-	.02666	.01171
i-C_4H_{10}	.63765	.70529	1.27987
n-C_4H_{10}	.03276	.01681	.03118
i-C_4H_8	.02020	.04297	.02960
HCHO	.02027	.01844	.02517
CH_3CHO	.00048	.00049	.00058
CH_3COCH_3	.00125	.00111	.00071
CH_3OH	.01013	.00734	.00869
H_2O	.12188	.13122	.11038
CH_3COOH	.00173	.00140	.00144

* C_3H_8 + C_3H_6

Table (2) (Continued)

Run No.	31	32	33
Reactor Temperature, °C.	350	350	350
Reactor Pressure, in.	29.55	29.6	29.55
Temperature of gases leaving soapmeter, °F.	80	82	80
Pressure of gases leaving soapmeter, in.	29.07	29.07	29.07
Gr. moles/hr. O_2 fed to reactor	.294	.2596	.251
Gr. moles/hr. i-C_4H_{10} fed to reactor	1.1566	1.0135	0.914
Gases leaving reactor	Gr. moles/hr.		
H_2	.00051	.00057	.00052
O_2	.18418	.16065	.15144
N_2	.01047	.00779	.00661
CH_4	.00449	.00842	.01875
CO	.02398	.02429	.02602
CO_2	.03194	.02167	.02178
C_2H_6	.00017	.00020	.00025
C_2H_4	.00056	.00089	.00148
C_3H_8	.01486	.01263	.01089
C_3H_6	.01397	.02018	.02112
i-C_4H_{10}	1.10016	.94626	.84665
n-C_4H_{10}	.02390	.02089	.01618
i-C_4H_8	.03081	.03556	.03431
HCHO	.01628	.01600	.01605
CH_3CHO	.00027	.00033	.00032
CH_3COCH_3	.00052	.00065	.00071
CH_3OH	.00546	.00610	.00635
H_2O	.09297	.09318	.09167
CH_3COOH	.00067	.00087	.00104

Table (2) (Continued)

Run No.	34	35	36
Reactor Temperature, °C.	350	375	375
Reactor Pressure, in.	29.8	30.4	30.4
Temperature of gases leaving soapmeter, °F.	78	78	75
Pressure of gases leaving soapmeter, in.	29.3	29.91	29.91
Gr. moles/hr. O_2 fed to reactor	.2202	.395	.3594
Gr. moles/hr. i-C_4H_{10} fed to reactor	.8253	1.55267	1.38391
Gases leaving reactor	Gr. moles/hr.		
H_2	.00357	.00069	.00052
O_2	.12957	.27599	.24252
N_2	.00574	.00814	.00360
CH_4	.01512	.00166	.00168
CO	.03234	.02528	.02167
CO_2	.01901	.03146	.03543
C_2H_6	.00020	.00010	.00003
C_2H_4	.00103	.00035	.00043
C_3H_8	.00993	.01451	.01256
C_3H_6	.01680	.01289	.01180
i-C_4H_{10}	.76965	1.48996	1.32096
n-C_4H_{10}	.01627	.03211	.03543
i-C_4H_8	.03077	.03686	.03337
HCHO	.01723	.02000	.01639
CH_3CHO	.00041	.00034	.00028
CH_3COCH_3	.00081	.00040	.00032
CH_3OH	.00704	.00526	.00367
H_2O	.08525	.11587	.11509
CH_3COOH	.00093	.00123	.00091

Table (2) (Continued)

Run No.	37	38	39
Reactor Temperature, °C.	375	375	375
Reactor Pressure, in.	30.04	30.4	30.34
Temperature of gases leaving soapmeter, °F.	77	78	78
Pressure of gases leaving soapmeter, in.	29.91	29.91	29.84
Gr. moles/hr. O_2 fed to reactor	.3054	.269	.2455
Gr. moles/hr. i-C_4H_{10} fed to reactor	1.20502	1.05891	.97404
Gases leaving reactor	Gr. moles/hr.		
H_2	.00044	.00061	.00019
O_2	.19175	.16506	.14400
N_2	.00194	.00158	.00208
CH_4	.00221	.00271	.00298
CO	.02581	.02554	.02261
CO_2	.02783	.02306	.02404
C_2H_6	.00006	.00005	.00006
C_2H_4	.00057	.00056	.00064
C_3H_8	.00988	.00851	.00761
C_3H_6	.01401	.01467	.01416
i-C_4H_{10}	1.14017	1.00608	.91261
n-C_4H_{10}	.02729	.02725	.02570
i-C_4H_8	.03304	.03432	.03332
HCHO	.01810	.01786	.01776
CH_3CHO	.00040	.00043	.00037
CH_3COCH_3	.00057	.00072	.00061
CH_3OH	.00475	.00728	.00585
H_2O	.11409	.10032	.09278
CH_3COOH	.00098	.00107	.00099

Table (2) (Continued)

Run No.	40	41	42
Reactor Temperature, °C.	375	375	375
Reactor Pressure, in.	30.35	29.1	29.1
Temperature of gases leaving soapmeter, °F.	78	80	78.5
Pressure of gases leaving soapmeter, in.	29.84	28.86	28.86
Gr. moles/hr. O_2 fed to reactor	.220	.6635	.551
Gr. moles/hr. i-C_4H_{10} fed to reactor	.86411	.98947	.84071
Gases leaving reactor	Gr. moles/hr.		
H_2	.00021	.00010	.00016
O_2	.12611	.45654	.36028
N_2	.00184	.01317	.00330
CH_4	.00370	.00217	.00256
CO	.02137	.04962	.05450
CO_2	.02266	.06373	.05358
C_2H_6	.00008	-	-
C_2H_4	.00061	.00127	.00126
C_3H_8	.00647	.00206	.00066
C_3H_6	.01290	.01642	.01735
i-C_4H_{10}	.80831	.90214	.74283
n-C_4H_{10}	.02158	.04153	.03878
i-C_4H_8	.03216	.03646	.03485
HCHO	.01066	.02747	.02381
CH_3CHO	.00031	.00064	.00087
CH_3COCH_3	.00055	.00129	.00163
CH_3OH	.00516	.00736	.00817
H_2O	.09472	.19327	.18020
CH_3COOH	.00082	.00206	.00188

Table (2) (Continued)

Run No.	43	44	45
Reactor Temperature, °C.	375	375	375
Reactor Pressure, in.	29.35	29.35	29.1
Temperature of gases leaving soapmeter, °F.	81	78	81
Pressure of gases leaving soapmeter, in.	29.23	29.23	29.06
Gr. moles/hr. O_2 fed to reactor	.4775	.6780	.363
Gr. moles/hr. i-C_4H_{10} fed to reactor	.72789	.98184	.52261
Gases leaving reactor	Gr. moles/hr.		
H_2	.00014	.00010	.00018
O_2	.30504	.46972	.21437
N_2	.00496	.00563	.01268
CH_4	.00199	.00147	.00308
CO	.04672	.05265	.04048
CO_2	.04626	.06241	.04337
C_2H_6	-	-	.00004
C_2H_4	.00110	.00099	.00103
C_3H_8	.01106	.01497	.00556
C_3H_6	.01388	.01595	.01205
i-C_4H_{10}	.66464	.90301	.46048
n-C_4H_{10}	.00987	.01340	.00742
i-C_4H_8	.02835	.03594	.02375
HCHO	.02129	.02795	.01678
CH_3CHO	.00038	.00060	.00046
CH_3COCH_3	.00088	.00097	.00108
CH_3OH	.00595	.00642	.00503
H_2O	.16677	.19904	.13793
CH_3COOH	.00155	.00206	.00135

Table (2) (Continued)

Run No.	46	47	48
Reactor Temperature, °C.	375	350	400
Reactor Pressure, in.	29.1	29.75	29.5
Temperature of gases leaving soapmeter, °F.	84	78	78
Pressure of gases leaving soapmeter, in.	29.08	29.14	29.4
Gr. moles/hr. O_2 fed to reactor	.287	.3756	.3690
Gr. moles/hr. i-C_4H_{10} fed to reactor	.43229	.56955	1.43471
Gases leaving reactor	Gr. moles/hr.		
H_2	.00019	.00026	.00036
O_2	.15852	.22011	.26870
N_2	.01047	.00220	.00280
CH_4	.00411	.00375	.00577
CO	.03371	.04784	.01542
CO_2	.03572	.03085	.03895
C_2H_6	.00005	-	-
C_2H_4	.00106	.00115	-
C_3H_8	.00435	.00459	.00577
C_3H_6	.01230	.01400	.00902
i-C_4H_{10}	.37760	.50791	1.40900
n-C_4H_{10}	.00896	.01092	.03463
i-C_4H_8	.02180	.02305	.02200
HCHO	.01510	.02196	.01307
CH_3CHO	.00026	.00076	.00003
CH_3COCH_3	.00073	.00177	.00003
CH_3OH	.00434	.01022	.00128
H_2O	.11582	.13617	.09024
CH_3COOH	.00108	.00179	.00060

Table (2) (Continued)

Run No.	49	50	51
Reactor Temperature, °C.	400	400	400
Reactor Pressure, in.	29.35	29.0	29.2
Temperature of gases leaving soapmeter, °F.	85	76	86
Pressure of gases leaving soapmeter, in.	29.24	28.88	29.14
Gr. moles/hr. O_2 fed to reactor	.286	.2507	.220
Gr. moles/hr. i-C_4H_{10} fed to reactor	1.13505	.99459	.84815
Gases leaving reactor	Gr. moles/hr.		
H_2	.00026	.00023	.00015
O_2	.19929	.16011	.13878
N_2	.00373	.00352	.00650
CH_4	.00740	.00746	.00763
CO	.01495	.01800	.01695
CO_2	.02854	.02759	.02649
C_2H_6	.00041	-	.00028
C_2H_4	.00024	.00017	.00047
C_3H_8	.02448	.00379	.01674
C_3H_6	.00831	.00833	.00881
i-C_4H_{10}	1.09097	.94155	.79656
n-C_4H_{10}	.02391	.03843	.01589
i-C_4H_8	.02107	.02242	.02415
HCHO	.01202	.01221	.01069
CH_3CHO	.00005	.00013	.00002
CH_3COCH_3	.00003	.00014	.00010
CH_3OH	.00130	.00217	.00112
H_2O	.08291	.07926	.07872
CH_3COOH	.00067	.00064	.00052

Table (2) (Continued)

Run No.	52	53	54
Reactor Temperature, °C.	400	400	400
Reactor Pressure, in.	29.15	29.55	29.95
Temperature of gases leaving soapmeter, °F.	80	78	77
Pressure of gases leaving soapmeter, in.	29.14	29.44	29.47
Gr. moles/hr. O_2 fed to reactor	.1793	.672	.47
Gr. moles/hr. i-C_4H_{10} fed to reactor	.69069	.97179	.72894
Gases leaving reactor	Gr. moles/hr.		
H_2	.00042	.00006	.00019
O_2	.10471	.44109	.27934
N_2	.00244	.00750	.00388
CH_4	.00790	.00491	.00649
CO	.01330	.03950	.04030
CO_2	.02798	.07808	.05822
C_2H_6	.00021	-	-
C_2H_4	.00036	.00089	.00090
C_3H_8	.01348	.01767	.01310
C_3H_6	.00781	.01614	.01854
i-C_4H_{10}	.64948	.87495	.64220
n-C_4H_{10}	.00910	.00584	.01793
i-C_4H_8	.02111	.05026	.03851
HCHO	.00897	.02839	.02119
CH_3CHO	.00006	.00054	.00003
CH_3COCH_3	.00012	.00107	.00067
CH_3OH	.00126	.00495	.00404
H_2O	.07194	.20583	.17386
CH_3COOH	.00047	.00192	.00136

Table (2) (Continued)

Run No.	55	56	57
Reactor Temperature, °C.	400	400	400
Reactor Pressure, in.	29.5	29.6	29.65
Temperature of gases leaving soapmeter, °F.	74	76	75.5
Pressure of gases leaving soapmeter, in.	29.49	29.58	29.57
Gr. moles/hr. O_2 fed to reactor	.2927	.2170	.2275
Gr. moles/hr. i-C_4H_{10} fed to reactor	.45083	.32032	.87373
Gases leaving reactor	Gr. moles/hr.		
H_2	.00012	.00007	.00004
O_2	.15087	.08264	.14039
N_2	.00176	.00086	.00130
CH_4	.00541	.00525	.00497
CO	.03532	.03105	.01255
CO_2	.04073	.04538	.03186
C_2H_6	-	-	-
C_2H_4	.00072	.00072	.00016
C_3H_8	.00764	.00521	.01511
C_3H_6	.00904	.01280	.00929
i-C_4H_{10}	.39951	.26637	.81801
n-C_4H_{10}	.00325	.00108	.01641
i-C_4H_8	.02219	.02627	.02980
HCHO	.01599	.01120	.00922
CH_3CHO	.00023	.00047	.00005
CH_3COCH_3	.00078	.00098	.00015
CH_3OH	.00337	.00272	.00160
H_2O	.12900	.12202	.08468
CH_3COOH	.00103	.00083	.00054

Table (2) (Continued)

Run No.	58	59
Reactor Temperature, °C.	400	375
Reactor Pressure, in.	29.45	29.95
Temperature of gases leaving soapmeter, °F.	81.5	80
Pressure of gases leaving soapmeter, in.	29.44	29.44
Gr. moles/hr. O_2 fed to reactor	.1092	.2180
Gr. moles/hr. i-C_4H_{10} fed to reactor	.43799	.83424
Gases leaving reactor	Gr. moles/hr.	
H_2	.00009	.00008
O_2	.05140	.12898
N_2	.00160	.00119
CH_4	.00660	.00743
CO	.00970	.01857
CO_2	.01811	.02641
C_2H_6	-	-
C_2H_4	.00027	.00019
C_3H_8	.00682	.01228
C_3H_6	.00943	.01341
i-C_4H_{10}	.40047	.76445
n-C_4H_{10}	.00351	.02559
i-C_4H_8	.02460	.03322
HCHO	.00502	.01287
CH_3CHO	.00002	.00019
CH_3COCH_3	.00013	.00046
CH_3OH	.00083	.00451
H_2O	.05732	.08694
CH_3COOH	.00032	.00083

APPENDIX II

EVALUATION OF REACTION RATE CONSTANT

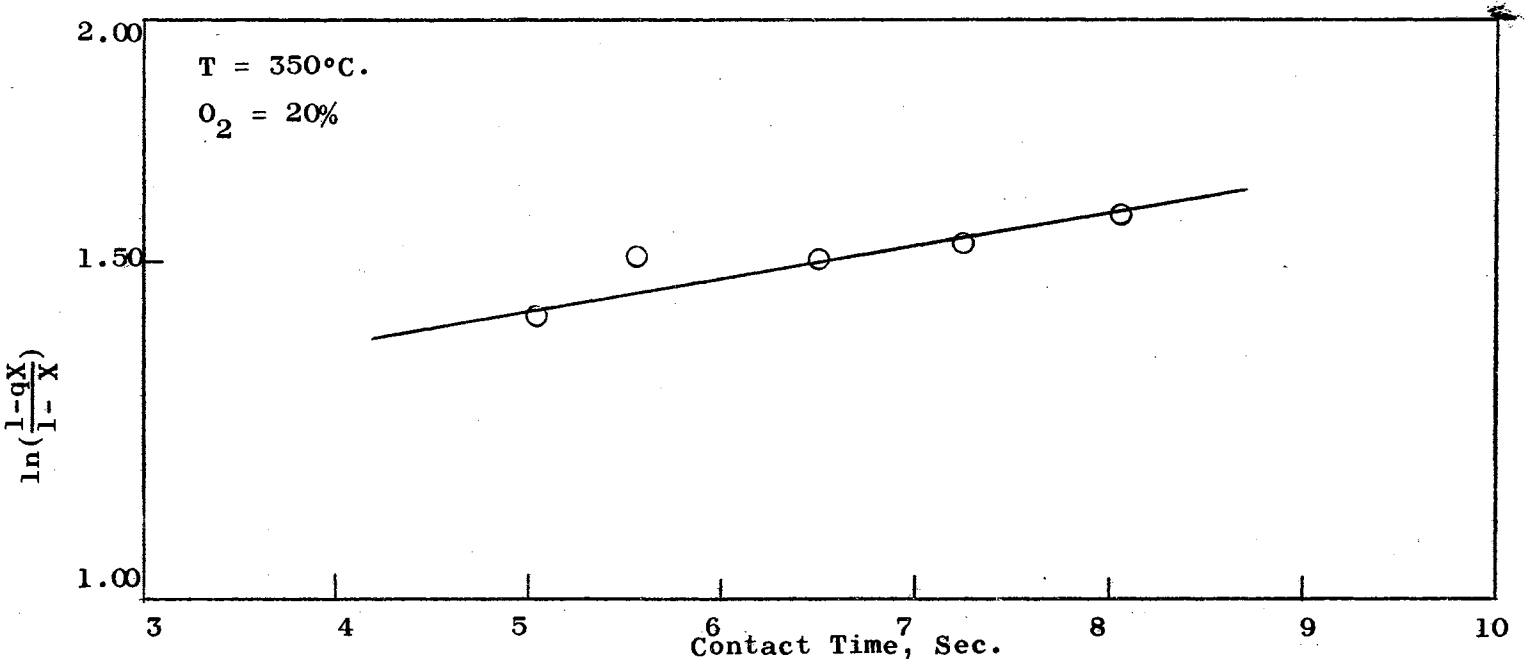

Figure 13

$\ln(\frac{1-qX}{1-X})$ Versus Contact Time, 350°C., 20% O_2

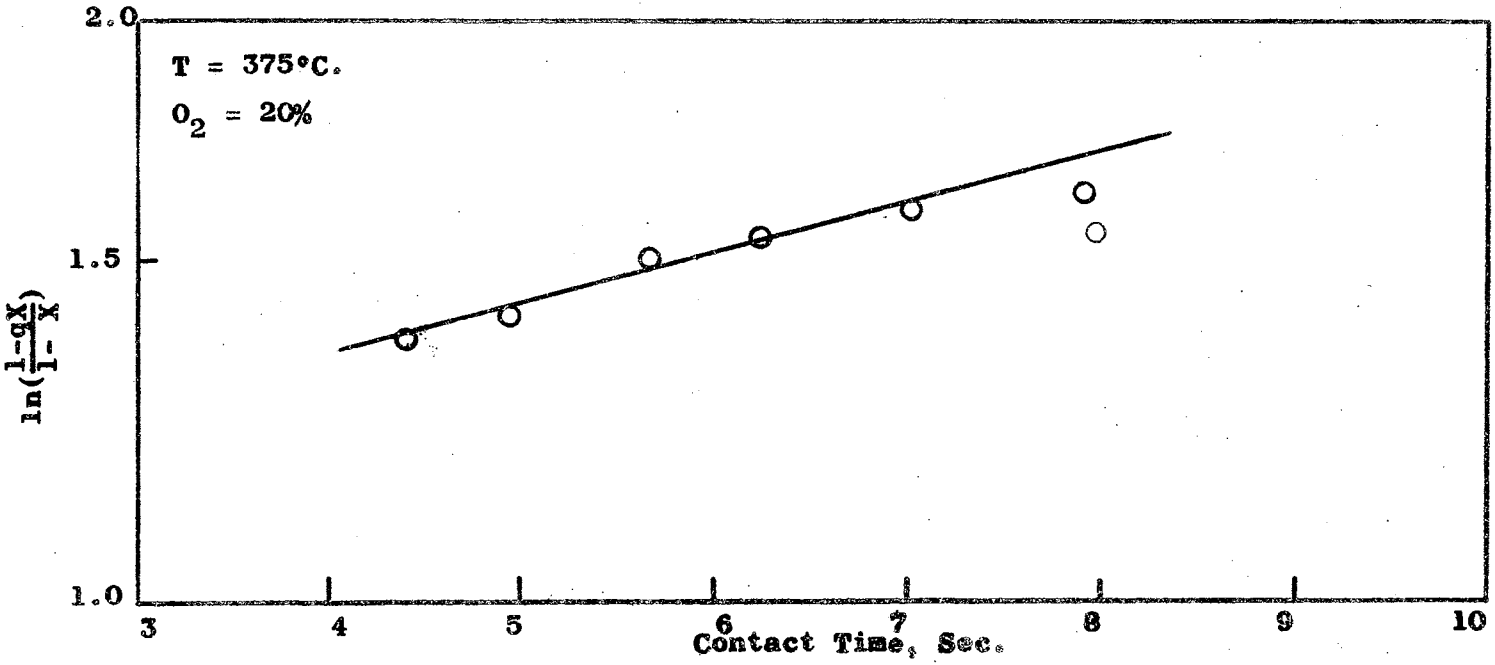

Figure 18

$\ln(\frac{1-qX}{1-X})$ Versus Contact Time, 375°C., 20% O_2

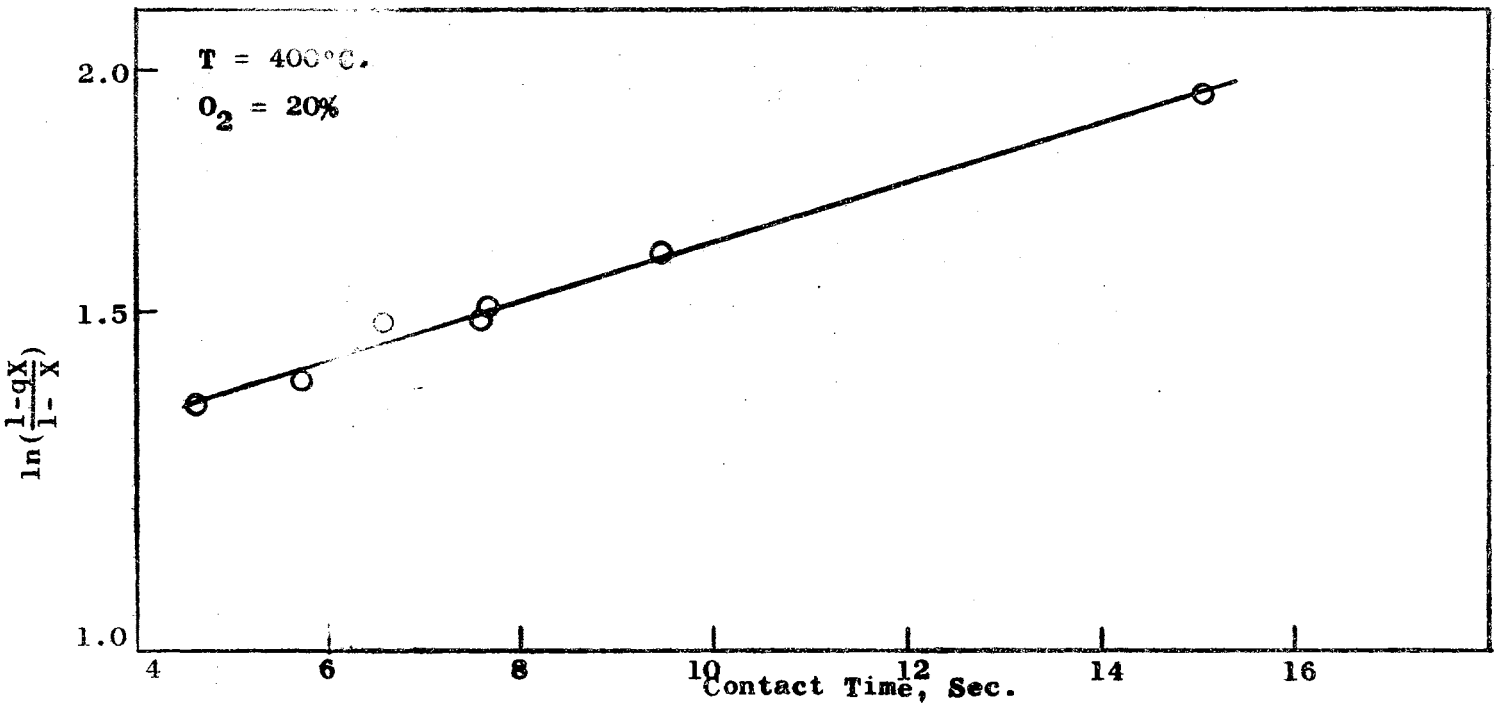

Figure 15

$\ln(\frac{1-qX}{1-X})$ Versus Contact Time, 400°C., 20% O_2

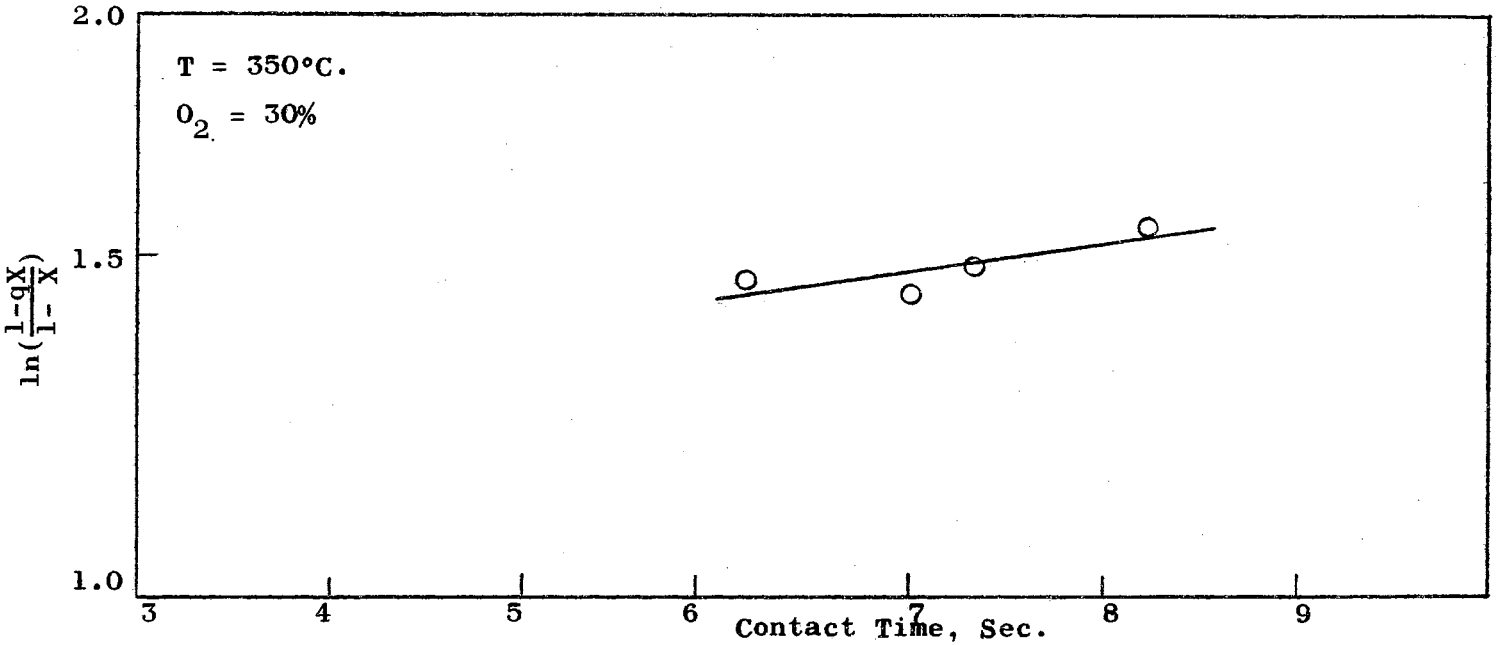

Figure 16

$\ln(\frac{1-qX}{1-X})$ Versus Contact Time, 350°C., 30% O_2

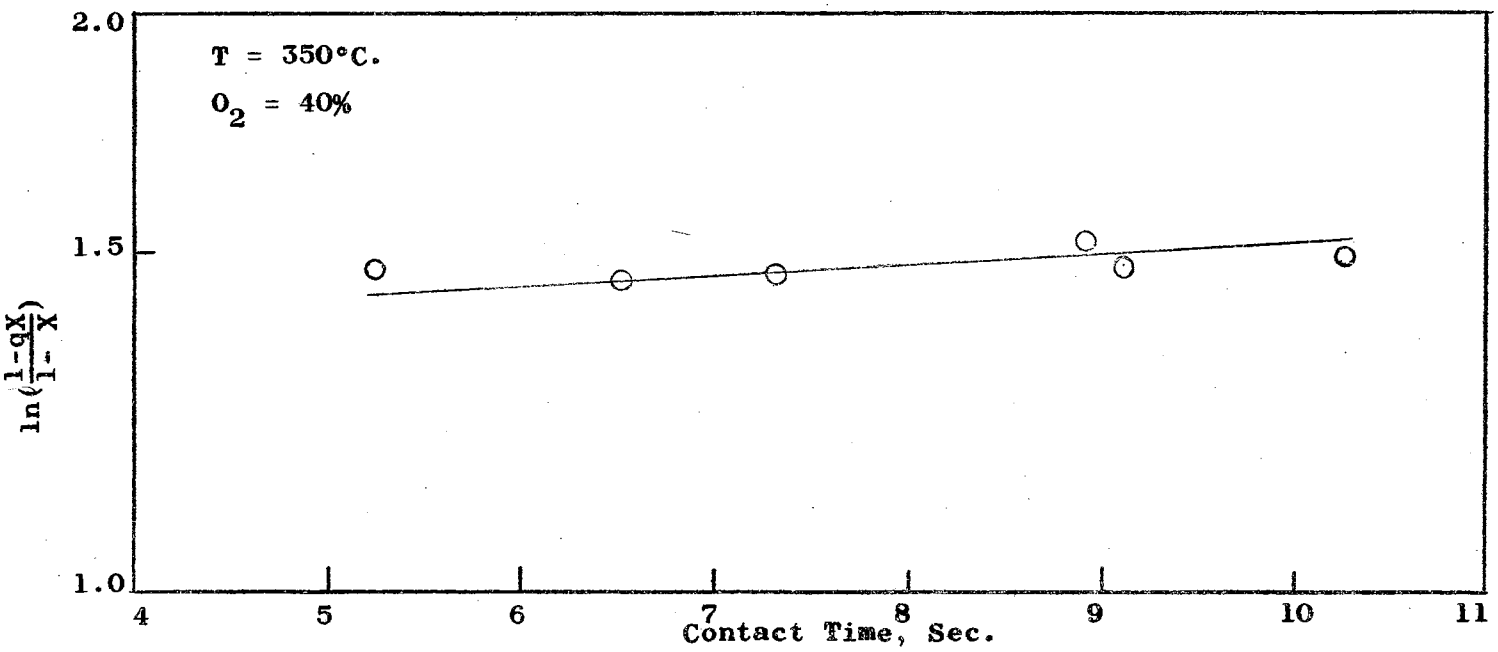

Figure 17

$\ln(\frac{1-qX}{1-X})$ Versus Contact Time, 350°C., 40% O_2

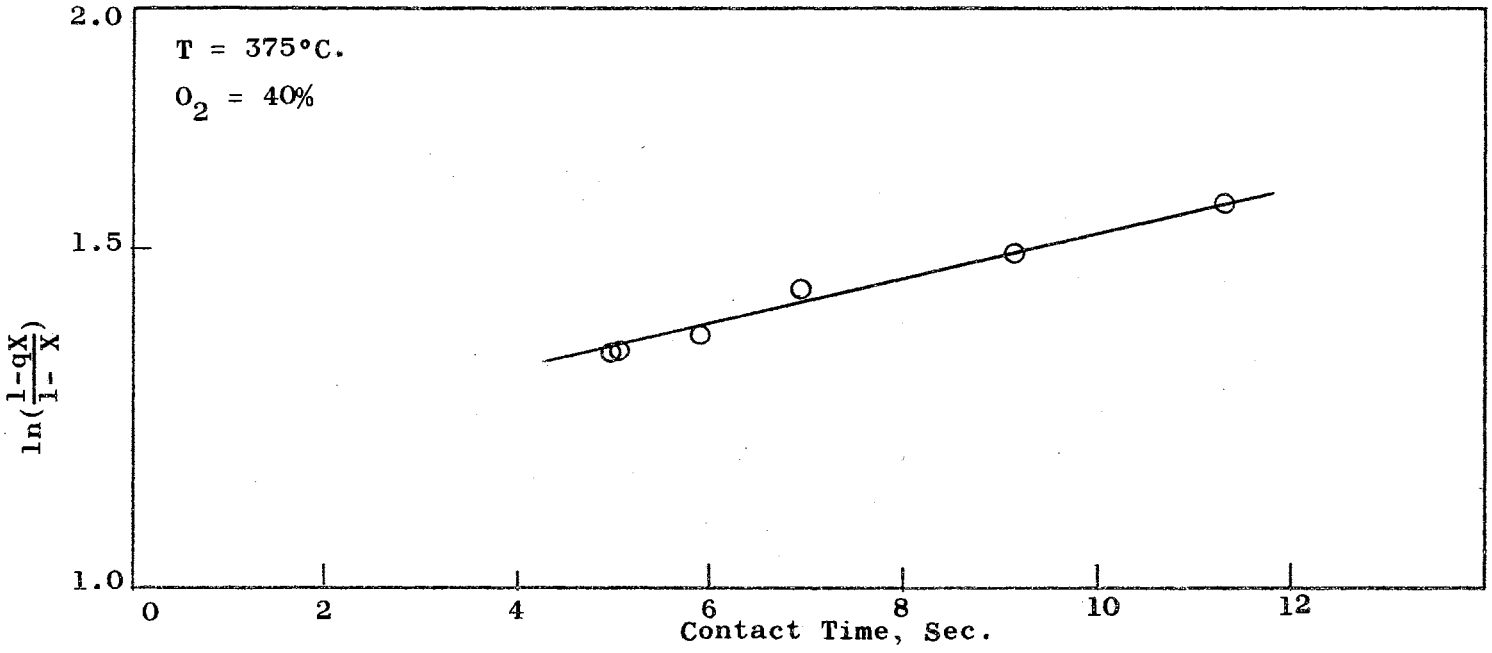

Figure 18

$\ln(\frac{1-qX}{1-X})$ Versus Contact Time, 375°C., 40% O_2

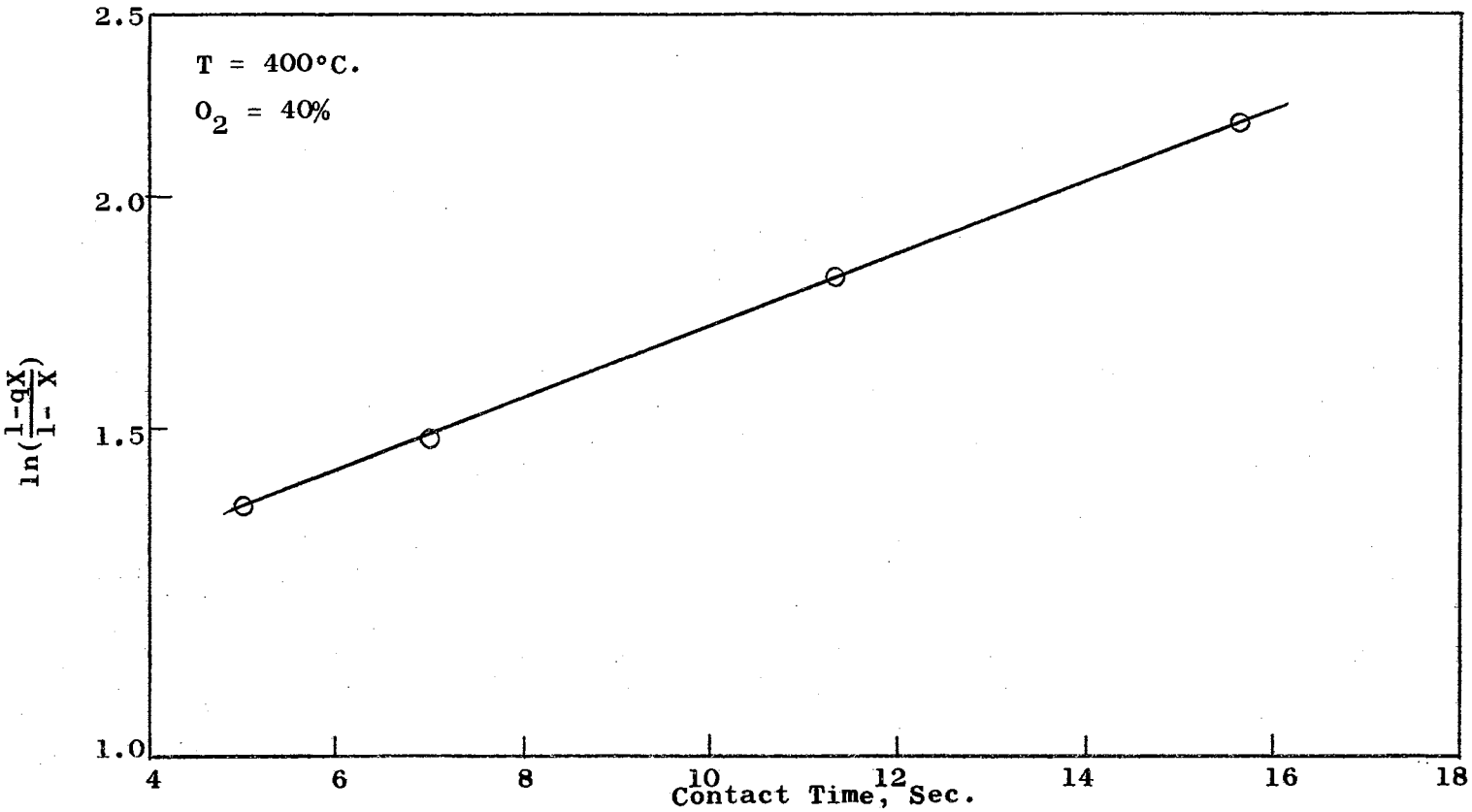

Figure 19

$\ln(\frac{1-qX}{1-X})$ Versus Contact Time , 400°C., 40% O_2

Table 3

Evaluation K in $\ln(\frac{1-qX}{1-X}) = kK$, 350°C., 20% O_2

θ^*	X	Y	$q=\frac{Y}{X}$	1-q	M	$\frac{N^o_{O_2}}{E}$	$(\frac{N^o_{O_2}}{E})^2$	K
5.05	.32179	.04248	.1320	.8680	4.025	.18954	.03592	0.1255
5.56	.37354	.04880	.1306	.8694	4.050	.18888	.03567	0.1256
6.50	.38116	.06634	.1740	.8260	4.025	.18844	.03551	0.1181
7.25	.39665	.07369	.1857	.8143	3.762	.19723	.03890	0.1192
8.06	.41158	.06743	.1638	.8362	3.878	.18948	.03590	0.1164
								0.1210 Av.

Table 4

Reaction Rate Constant at 350°C., 20% O_2

θ	q	1-qX	1-X	$\frac{1-qX}{1-X}$	K'	$K_{av.}$	$k_{av.}$
5.05	0.1320	0.95752	0.67821	1.412			
5.56	0.1306	0.95122	0.62646	1.518			
6.50	0.1740	0.93368	0.61884	1.509	0.0383	0.1210	0.3166
7.25	0.1847	0.92635	0.60335	1.535			
8.06	0.1638	0.93258	0.58842	1.585			

* Contact Time

Table 5

Evaluation of K at 375°C., 20% O_2

θ	X	Y	q	1-q	M	$\frac{N^o_{O_2}}{E}$	$(\frac{N^o_{O_2}}{E})^2$	K
4.40	0.30129	0.04039	0.134	0.8660	4.025	0.19051	0.03629	0.1265
4.94	0.32521	0.04549	0.1399	0.8601	3.963	0.19353	0.03746	0.1277
5.67	0.37213	0.05382	0.1446	0.8554	4.050	0.18923	0.03581	0.1241
6.21	0.38639	0.04989	0.1291	0.8709	4.025	0.18711	0.03501	0.1227
7.01	0.41344	0.06307	0.1525	0.8475	4.076	0.18758	0.03519	0.1216
7.90	0.42677	0.06458	0.1513	0.8487	4.025	0.18800	0.03534	0.1207
7.994	0.40834	0.08350	0.2048	0.7952	3.911	0.19163	0.03672	0.1142

Table 6

Reaction Rate Constant, k, at 375°C., and 20% O_2

θ	q	1-qX	1-X	$\frac{1-qX}{1-X}$	K'	$K_{av.}$	$k_{av.}$
4.40	0.134	0.95963	0.69871	1.373			
4.94	0.1399	0.95450	0.67479	1.415			
5.67	0.1446	0.94619	0.62787	1.507			
6.21	0.1291	0.95012	0.61361	1.548	0.0619	0.1225	0.5053
7.01	0.1525	0.93700	0.58656	1.597			
7.90	0.1513	0.93543	0.56323	1.632			
7.994	0.2048	0.91637	0.59166	1.549			

Table 7

Evaluation of K at 400°C. and 20% O_2

θ	X	Y	q	1-q	M	$\frac{N^o_{O_2}}{E}$	$(\frac{N^o_{O_2}}{E})^2$	K
4.609	0.27181	0.02413	0.0887	0.9113	4	0.19333	0.03738	0.1495
5.738	0.30318	0.03884	0.1281	0.8719	4.055	0.18809	0.03538	0.1251
6.592	0.36135	0.05333	0.1476	0.8524	4.066	0.18904	0.03574	0.1239
7.597	0.36918	0.06083	0.1647	0.8353	3.950	0.19121	0.03656	0.1206
9.452	0.4160	0.05967	0.1434	0.8566	3.95	0.19052	0.0363	0.1228
15.064	0.5293	0.08566	0.1618	0.8382	4.107	0.18315	0.03354	0.1155
7.629	0.3829	0.06375	0.1665	0.8335	3.936	0.19343	0.03741	0.1227
								0.1257 Av.

Table 8

Reaction Rate Constant, k, at 400°C., and 20% O_2

θ	q	1-qX	1-X	$\frac{1-qX}{1-X}$	K'	$K_{av.}$	$k_{av.}$ sec.$^{-1}$
4.609	0.0887	0.97589	0.72819	1.340			
5.738	0.1281	0.96116	0.69682	1.379			
6.592	0.1476	0.94667	0.63865	1.482			
7.597	0.1647	0.9392	0.63082	1.489	0.0349	0.1257	0.2776
9.452	0.1434	0.94035	0.584	1.61			
15.064	0.1618	0.91436	0.4707	1.943			
7.629	0.1665	0.93624	0.6171	1.517			

Table 9

Evaluation of K at 350°C. and 30% O_2

θ	X	Y	q	1-q	M	$\frac{N^o_{O_2}}{E}$	$(\frac{N^o_{O_2}}{E})^2$	K
6.16	0.3718	0.0806	0.2165	0.7835	2.333	0.28119	0.07907	0.1445
7.01	0.35918	0.082	0.2283	0.7717	2.361	0.27591	0.07612	0.1387
8.24	0.41849	0.09199	0.2198	0.7802	2.333	0.27945	0.07812	0.1422
7.32	0.38373	0.11195	0.291	0.709	2.333	0.27324	0.07464	0.140
								0.1413 Av.

Table 10

Reaction Rate Constant, k, at 350°C. and 30% O_2

θ	q	1-qX	1-X	$\frac{1-qX}{1-X}$	K'	$K_{av.}$	$k_{av.}$
6.16	0.2165	0.91951	0.6282	1.464			
7.01	0.2283	0.918	0.64082	1.433	0.0336	0.1413	0.238
8.24	0.2193	0.90823	0.58151	1.562			
7.32	0.2190	0.91596	0.61627	1.486			

Table 11

Evaluation of K at 350°C. and 40% O_2

θ	X	Y	q	1-q	M	$\frac{N^o_{O_2}}{E}$	$(\frac{N^o_{O_2}}{E})^2$	K
5.25	0.37904	0.08518	0.2247	0.7753	1.5	0.37636	0.14137	0.1644
6.52	0.38116	0.09841	0.258	0.742	1.5	0.37237	0.1386	0.1542
7.31	0.38408	0.09827	0.2558	0.7442	1.5	0.37123	0.1378	0.1549
8.917	0.41397	0.1082	0.2614	0.7386	1.553	0.36141	0.1306	0.1498
10.26	0.41921	0.1341	0.3199	0.6801	1.5	0.36376	0.1318	0.1345
9.13	0.39513	0.1040	0.2630	0.7370	1.525	0.36486	0.1331	0.1496
								0.1502 Av.

Table 12

Reaction Rate Constant, k, at 350°C. and 40% O_2

θ	q	1-qX	1-X	$\frac{1-qX}{1-X}$	K'	$K_{av.}$	$k_{av.}$
5.25	0.2247	0.91483	0.62096	1.473			
6.52	0.258	0.90166	0.61884	1.457			
7.31	0.2558	0.90175	0.61592	1.464	0.0154	0.1502	0.102
8.917	0.2614	0.89179	0.58603	1.52			
10.26	0.3199	0.8959	0.58079	1.491			
9.13	0.263	0.89608	0.60487	1.481			

Table 13

Evaluation of K at 375°C. and 40% O_2

θ	X	Y	q	1-q	M	$\frac{N^o_{O_2}}{E}$	$(\frac{N^o_{O_2}}{E})^2$	K
4.97	0.31192	0.08825	0.2829	0.7171	1.518	0.3651	0.1333	0.1451
5.9	0.34613	0.11642	0.3363	0.6637	1.553	0.36092	0.1308	0.1343
6.925	0.36117	0.08689	0.2406	0.7594	1.562	0.35880	0.1288	0.1528
9.17	0.40945	0.11888	0.2903	0.7097	1.474	0.36773	0.1352	0.1414
11.31	0.44766	0.12650	0.2826	0.7174	1.544	0.35600	0.1267	0.1403
5.01	0.3072	0.08029	0.2614	0.7386	1.486	0.37391	0.1398	0.1534
								0.1446 Av.

Table 14

Reaction Rate Constant, k, at 375°C. and 40% O_2

θ	q	1-qX	1-X	$\frac{1-qX}{1-X}$	K'	$K_{av.}$	$k_{av.}$
5.97	0.2829	0.91207	0.68808	1.3255			
5.9	0.3363	0.8836	0.65387	1.3513			
6.925	0.2406	0.9131	0.63883	1.4293			
9.17	0.2903	0.88114	0.59055	1.492	0.02790	0.1446	0.1930
11.31	0.2826	0.87349	0.55234	1.5814			
5.01	0.2614	0.9197	0.6928	1.3275			

Table 15

Evaluation of K at 400°C. and 40% O_2

θ	X	Y	q	1-q	M	$\frac{N^o_{O_2}}{E}$	$(\frac{N^o_{O_2}}{E})^2$	K
5.093	0.34361	0.09965	0.290	0.710	1.483	0.37759	0.1426	0.1501
7.01	0.40566	0.1190	0.2933	0.7067	1.59	0.35583	0.1266	0.1422
11.346	0.511	0.11383	0.2226	0.7774	1.578	0.35395	0.1255	0.1537
15.664	0.61917	0.1684	0.272	0.728	1.511	0.35232	0.1241	0.1365
								0.1456 Av.

Table 16

Reaction Rate Constant, k, at 400°C. and 40% O_2

θ	q	1-qX	1-X	$\frac{1-qX}{1-X}$	K'	$K_{av.}$	$k_{av.}$
5.093	0.290	0.90035	0.65639	1.372			
7.01	0.2933	0.88102	0.59434	1.482			
11.346	0.2226	0.88625	0.489	1.812	0.0448	0.1456	0.3080
15.664	0.272	0.38159	0.38083	2.183			

Table 17

Reaction Rate Constants

T, °C	$\%O_2$ Initial	$k_{exp.}$, sec^{-1}
350	20	0.3166
375	20	0.5053
400	20	0.2776
350	30	0.238
350	40	0.102
375	40	0.1930
400	40	0.3080

APPENDIX III

CALIBRATION CURVES

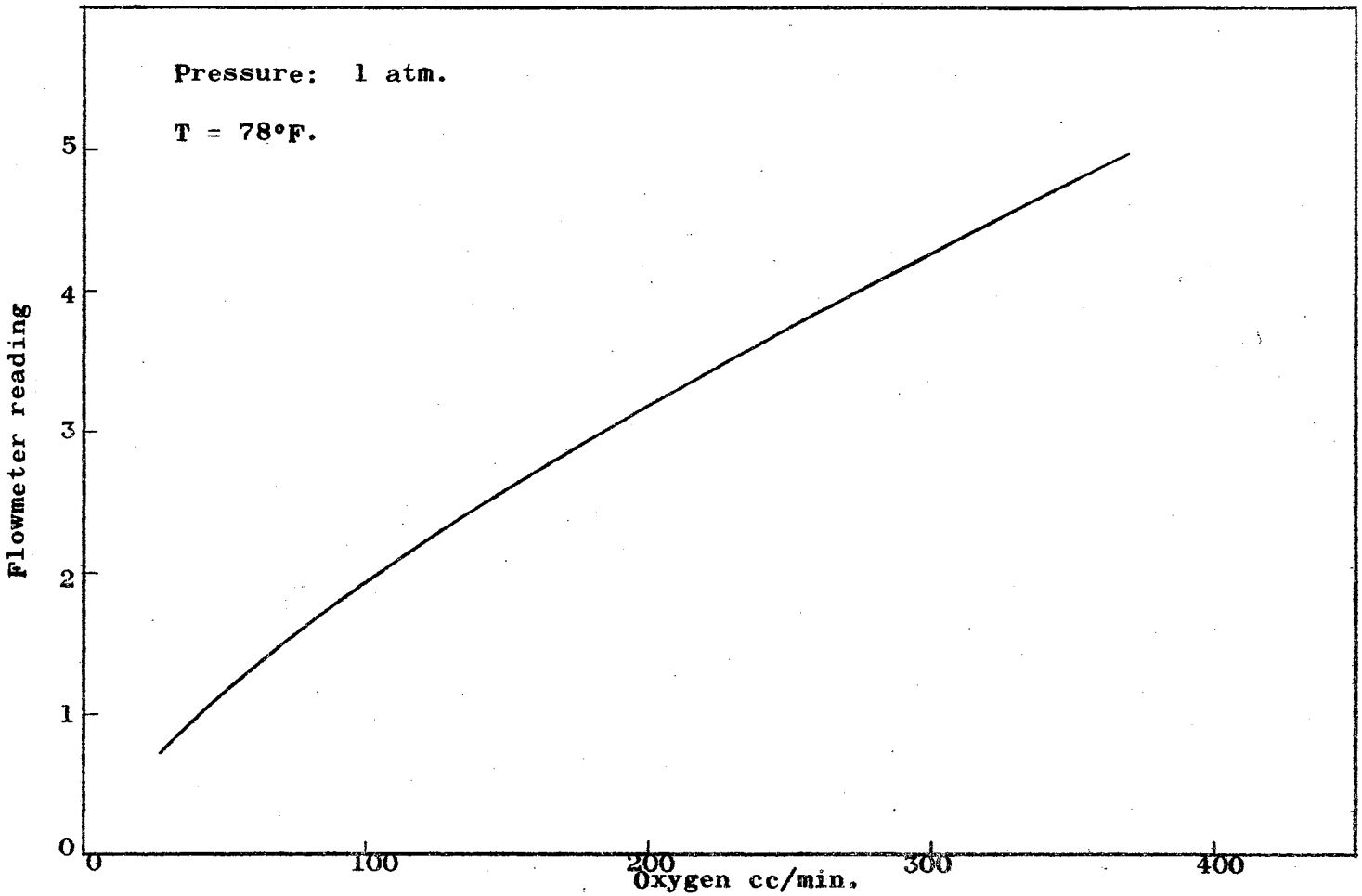

Figure 20

O_2 Flow Rate Calibration Curve

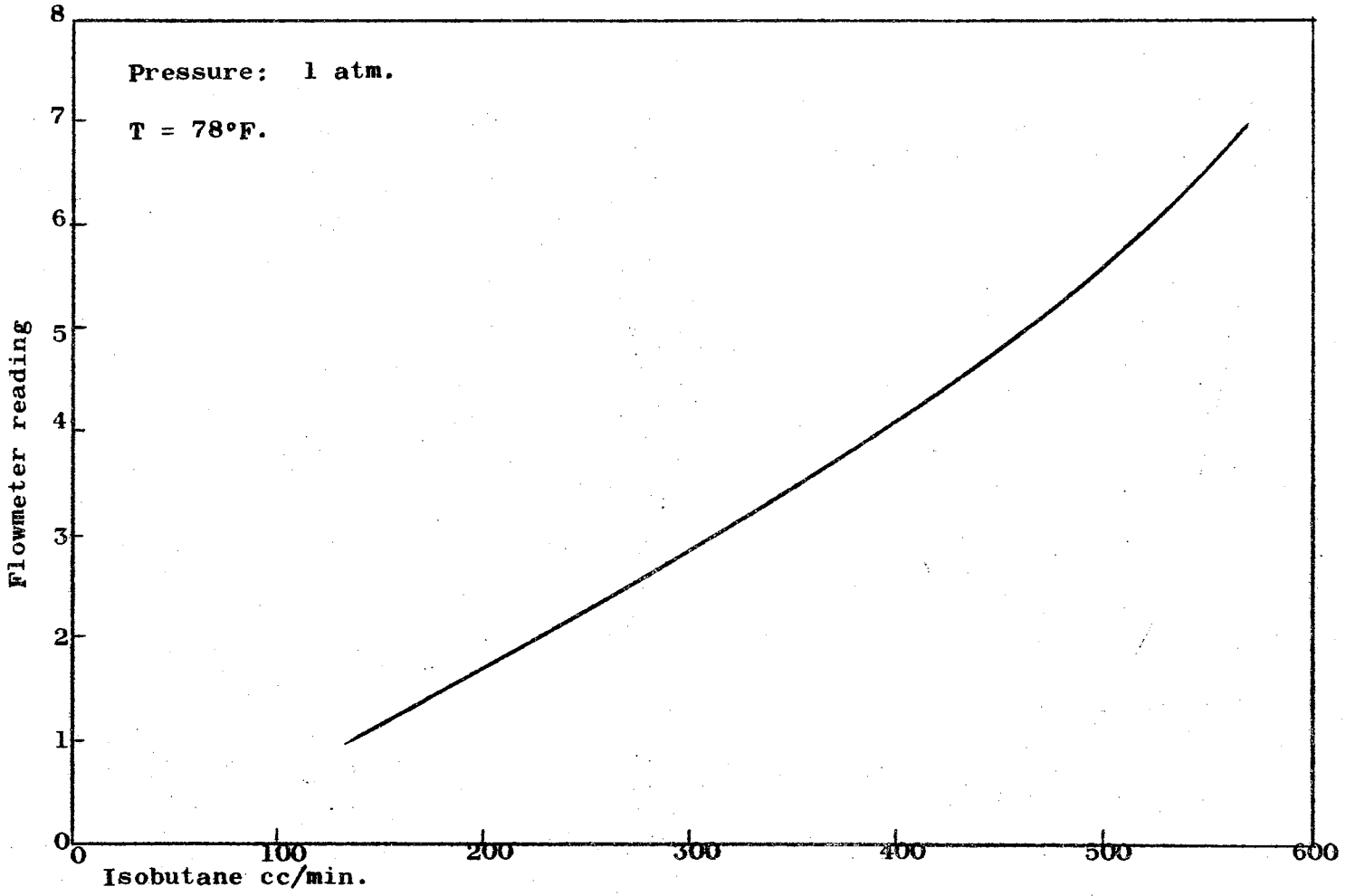

Figure 21

Isobutane Flow Rate Calibration Curve

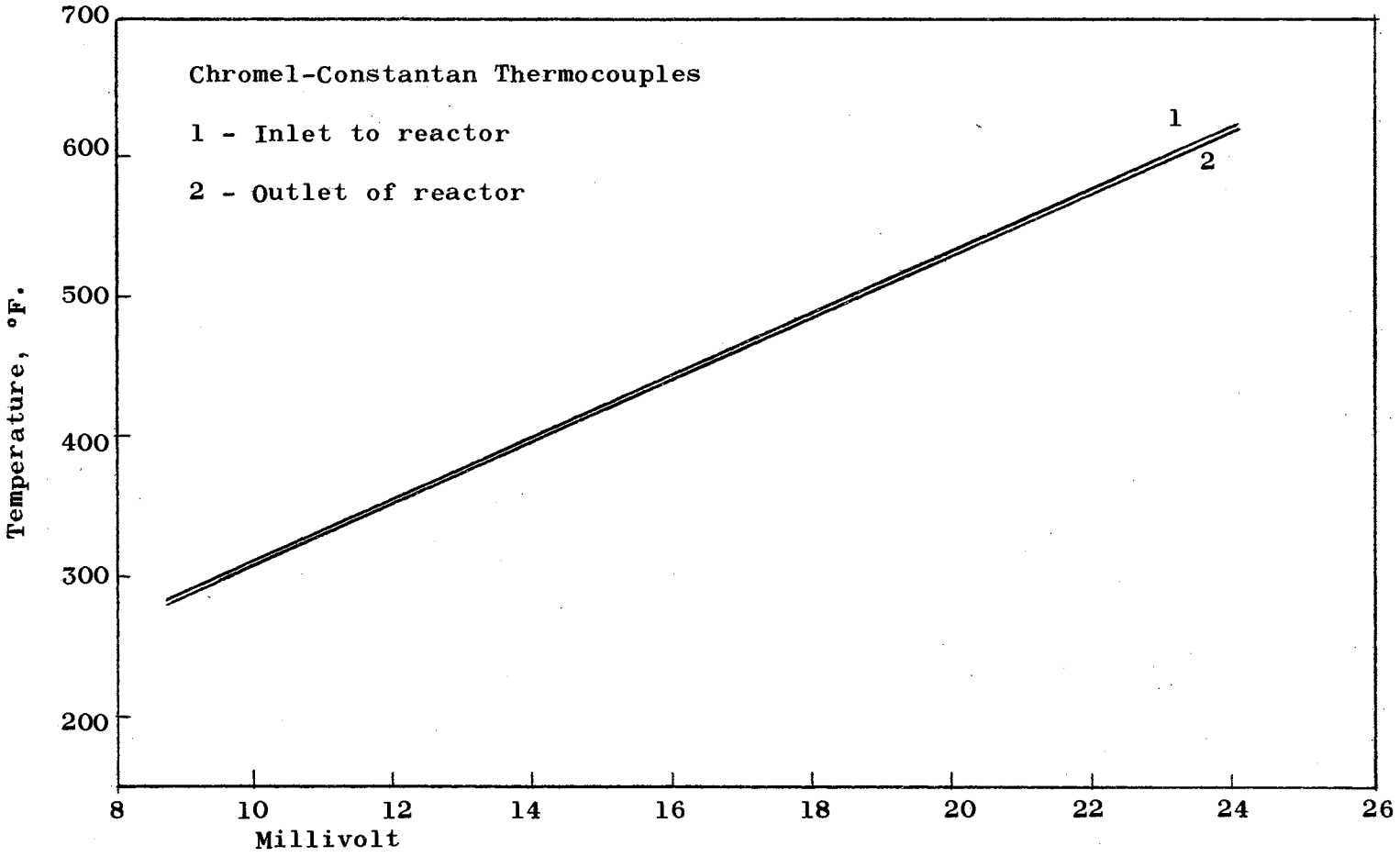
Chromel-Constantan Thermocouples
1 - Inlet to reactor
2 - Outlet of reactor
1
2
Temperature, °F.
700
600
500
400
300
200
8
10
12
14
16
18
20
22
24
26
Millivolt

Figure 22

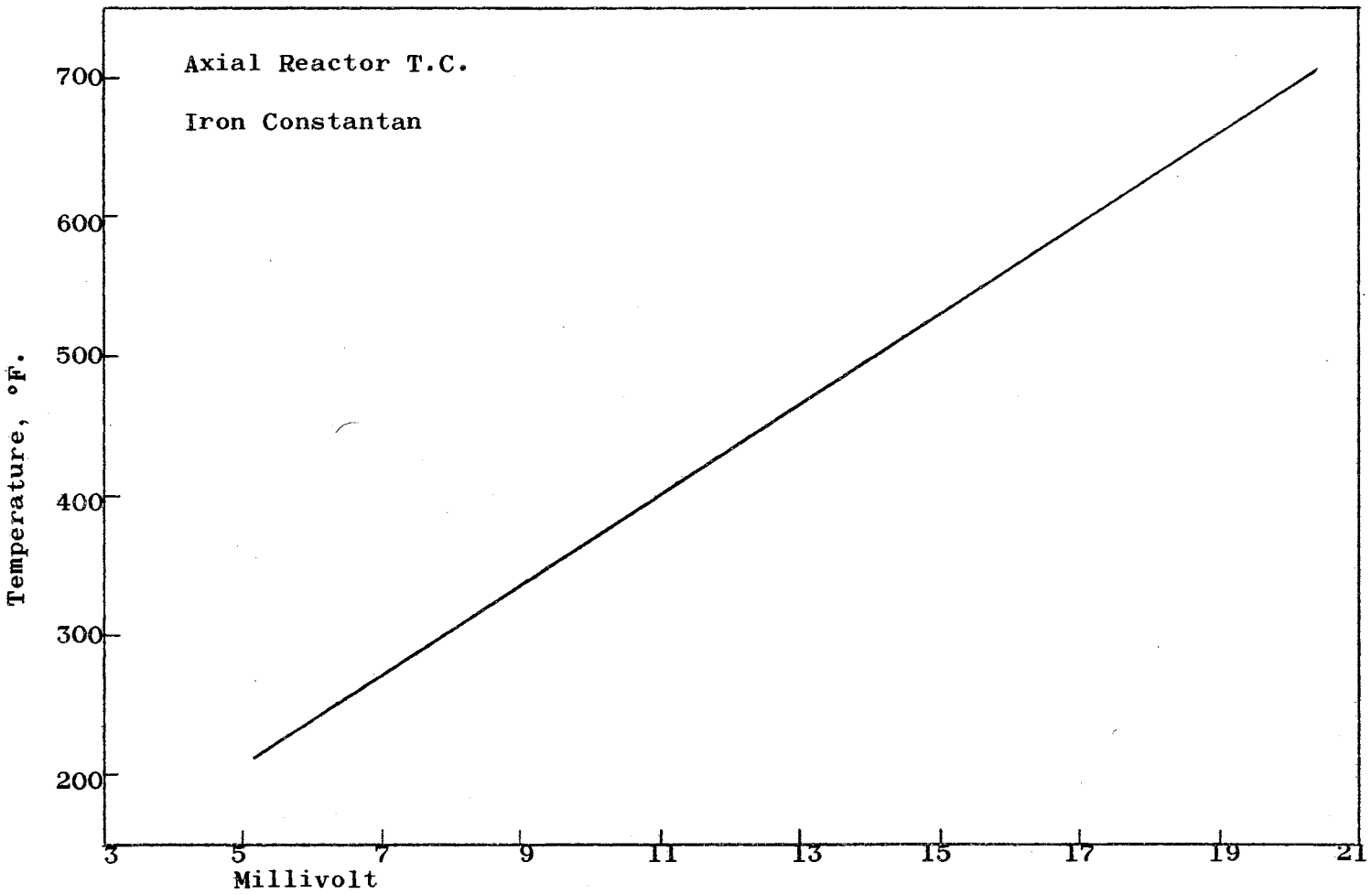
Axial Reactor T.C.
Iron Constantan
Temperature, °F.
700
600
500
400
300
200
3
5
7
9
11
13
15
17
19
21
Millivolt

Figure 23

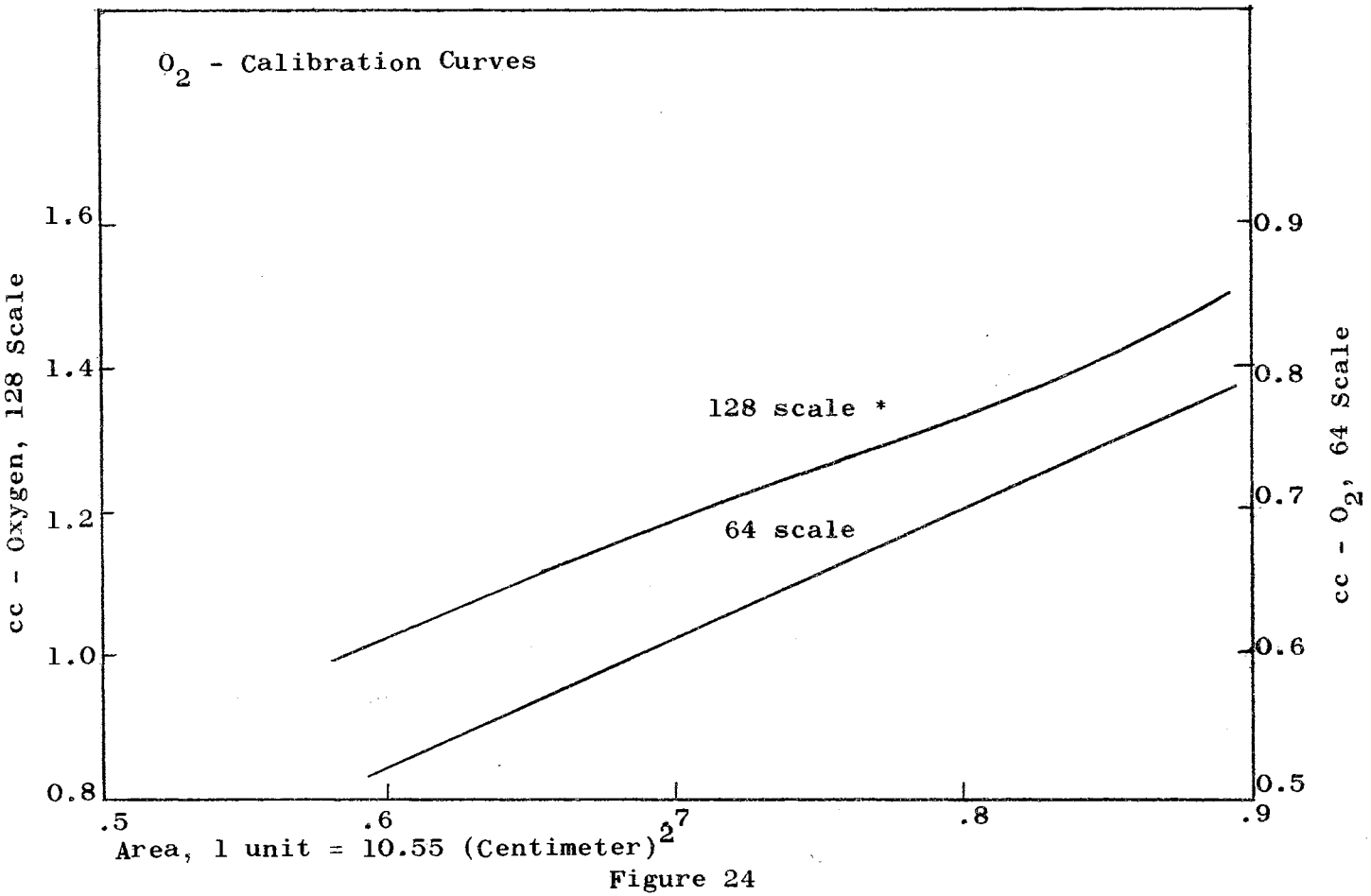

Figure 24

* Gas Chromatography Scale

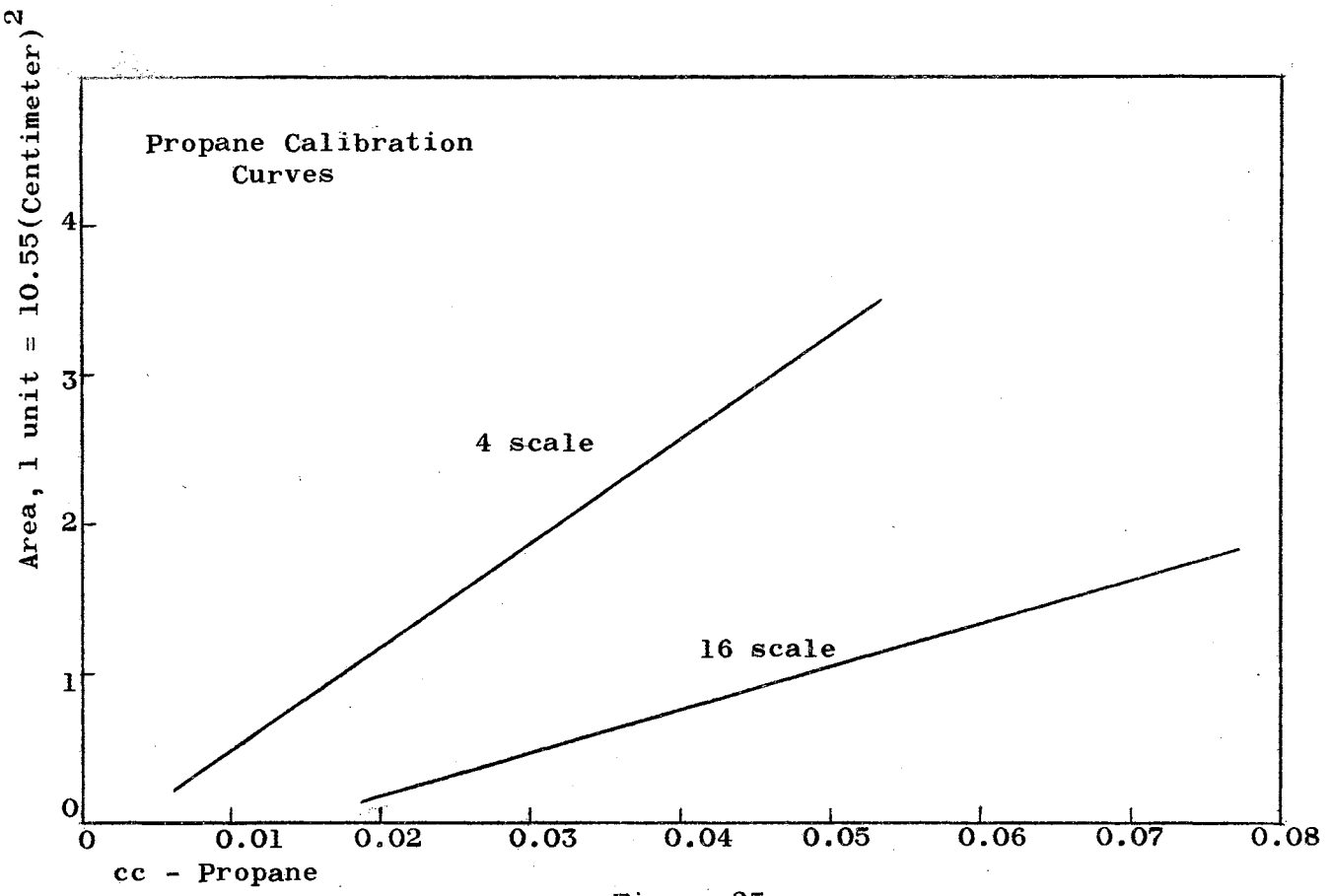
Propane Calibration
Curves
Area, 1 unit = 10.55(Centimeter)^2
4
3
2
1
0
4 scale
16 scale
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
cc - Propane

Figure 25

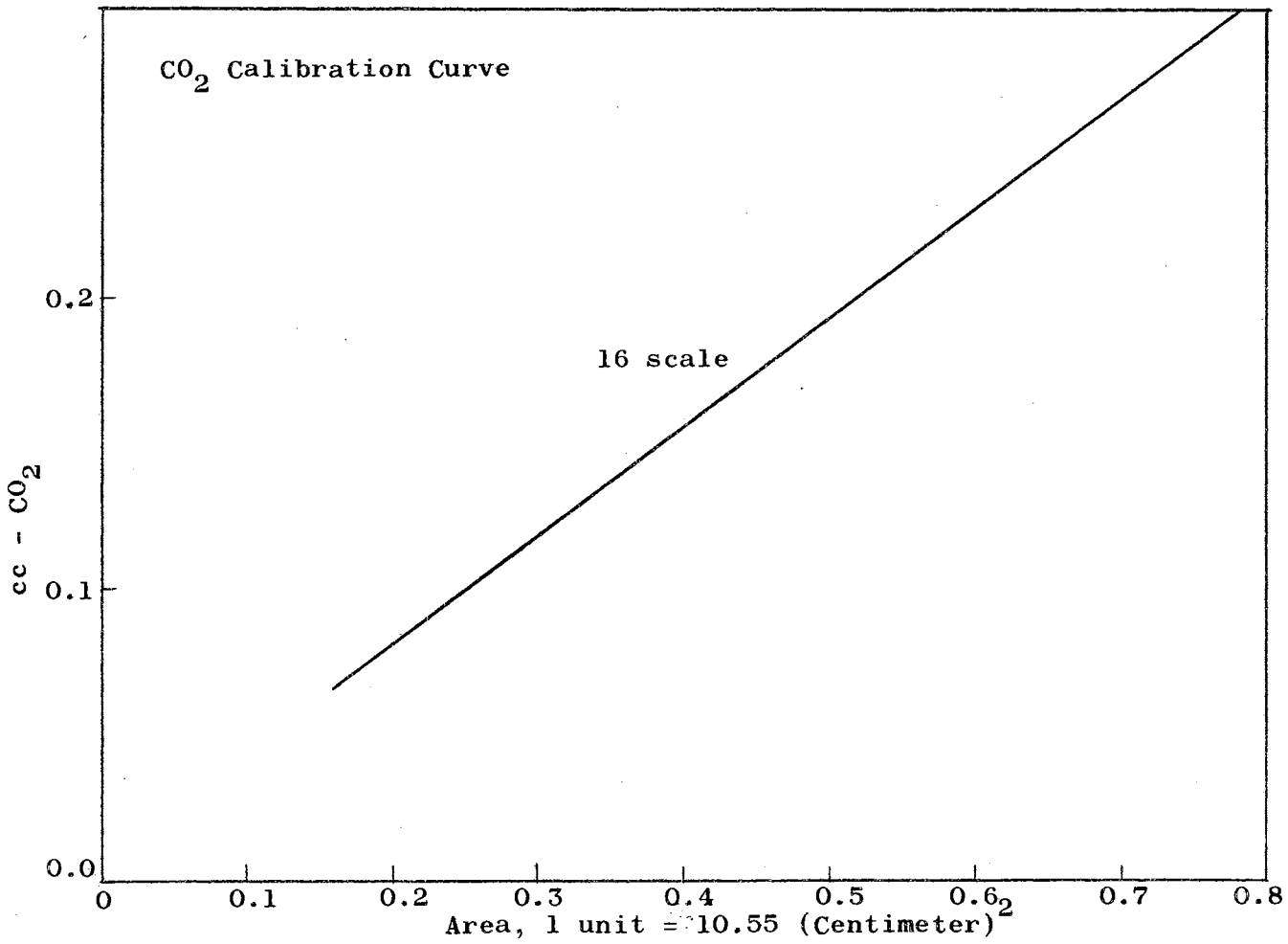
CO_2 Calibration Curve
16 scale
cc - CO_2
0.0
0.1
0.2
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
Area, 1 unit = 10.55 (Centimeter)^2

Figure 26

APPENDIX IV

PROGRAMMED GAS CHROMATOGRAPHY UNIT

APPENDIX IV

PROGRAMMED GAS CHROMATOGRAPHY

Introduction-

Programmed gas chromatography is an extension of isothermal gas chromatography and resulted from the limitation of constant temperature for the analysis of complex mixtures containing low-medium-high boiling constituents. The convenient spread of elution peaks and increased overall resolution obtained by increasing column temperature have proved to be much superior for many types of sample mixtures.

In programmed gas chromatography the temperature of the entire column increases linearly with time at a predetermined rate.

Theoretical Principles-

Programmed gas chromatography has been the subject of many papers in recent years. Martin et al (4)* showed graphically the relation between programmed and isothermal gas chromatography, Habgood and Harris (3) have reported on the mathematical investigation of programmed temperature gas chromatography and have derived an equation showing the relationship between isothermal retention volumes and retention volumes under linear temperature programming.

---

*These references are at the end of this section.

Using a different approach, Rowan (5) derived an expression which relates temperature rise, flow rate, starting and peak temperatures, and slope, and intercept of the plot of logarithm of the retention volume versus the reciprocal of the absolute temperature.

Giddings (2) has presented a theoretical analysis of programmed gas chromatography showing the influence of molecular structure, heating rate, gas velocity and other parameters on the retention times and temperatures of various solutes.

The behavior of the solute has also been described in detail by Dal Nogare and Langlois (1). They show the dependence of retention time on heating rate, mass flow rate of carrier gas, and starting temperature. The interpretation of plate height and column efficiency has been discussed by Stewart (6).

Operation-

In order to achieve best results, several conditions should be satisfied. The programmed temperature technique requires that column temperature be controlled independently of the detector. It is desired that the detector block be maintained at a high constant temperature and not be affected by column temperature changes. The carrier gas at constant pressure from a reducing valve must be maintained at constant flow rate by a flow controller, even though the resistance to flow in the column changes. A good baseline can be obtained if impurities such as CO_2, H_2O are removed from the helium. Furthermore, it is necessary to maintain the pressure on the reference and detector side constant. This is accomplished by splitting helium

flow to the reference and sample side and expelling to the atmosphere. Figure (27) shows the programmed gas chromatography unit used in this investigation.

Summary-

The ability to increase linearly the temperature of a gas chromatography column during an analysis has broadened the scope of gas chromatography. It has become a simple research analytical tool. Programming allows the components with a very strong affinity for column packing to emerge in a reasonable length of time. This system is invaluable in the following applications:

1. Routine analysis of mixtures containing material with widely different boiling point.
2. The simple analysis of a completely unknown sample.
3. The initial analysis of a sample to determine proper conditions for additional gas chromatography studies.
4. The analysis of samples by gas solid chromatography.
5. The analysis of trace high boiling components in low boiling components (solvents).
6. The collection of separated fractions for study by other techniques.
7. The analysis of temperature sensitive materials.

REFERENCES

1. **Dal Nogare, S., and Langlois, M. E., Anal. Chem. Vol. 32,** 767, 1960.

2. **Giddings, J. C., J. Chromatog.** Vol. 4, No. 20, 1960.

3. **Habgood, H. W., and Harris, W. E., Anal. Chem. Vol. 32,** 450, 1960.

4. **Martin, A. J., Bennet,** C. E., and Martinez, F. W., Jr., in "Gas Chromatography 1961", edited by Moebels, Wall, and Brenner. (Academic Press, New York, 1961).

5. **Rowan, R., Jr., Anal. Chem. Vol. 33,** 510, 1961.

6. **Stewart, G. H., Anal. Chem., Vol. 32,** 1205, 1960.

7. **Szymanski,** H. A., Progress in Industrial Gas Chromatography, 1961.

8. **Rosie,** D. M., Anal. Chem. 31, 230, 1959.

Chromatography Calculation for Run No. 46

Column	Component	Area *	cc/5cc Sample	Method
	H_2	.05 x 2	.00145	$\frac{.05 \times 2}{.7 \times 128} = 1.185$
	O_2	.7 x 128	1.185	Direct from calib. curve
M.S.	N_2	.74 x 8	.0783	$\frac{.74 \times 8}{.7 \times 128} \times 1.185$
	CH_4	.29 x 8	.0307	$\frac{.29 \times 8}{.7 \times 128} \times 1.185$
	CO	1.19 x 16	.252	$\frac{1.19 \times 16}{.7 \times 128} \times 1.185$
S.G.	CO_2	.68 x 16	.267	Direct
	C_2H_6	.03 x 2	.00035	$\frac{.03 \times 2}{2.06 \times 4} (\frac{65}{51}).0325$**
	C_2H_4	.74 x 2	.00795	$\frac{.74 \times 2}{2.06 \times 4} (\frac{65}{49}).0325$**
Act. Al.	C_3H_8	2.06 x 4	.0324	Direct
	C_3H_6	2.83 x 8	.092	$\frac{2.83 \times 8}{2.06 \times 4} (\frac{65}{63}) .0325$**
	$isoC_4H_8$	3.26 x 16	.163	$\frac{3.25 \times 16}{2.06 \times 4} (\frac{65}{82}) .0325$**

Continued

Column	Component	Area *	cc/5cc Sample	Method
	$n\text{-}C_4+isoC_4H_8$	2.42 x 4	.23	$\frac{2.42 \times 4}{2.01 \times 2}$ $(\frac{64}{84})$ .01245**
D.N.P.	$C_3H_8+C_3H_6$	2.01 x 2	.1245	From Act. Al. Col.
	$n\text{-}C_4H_{10}$		.067	By substraction

Isobutane = 2.82275cc = 5 - sum above components

Liquid Wt. Fractions

Column	Component	Area	Wt.%
	Acetaldehyde	.4	.509
	Acetone	1.46	1.856
Di-n-O-P	Methanol	4.8	6.102
	H_2O	72	91.533

where Wt.% component i = $\frac{\text{area i}}{\text{Total area}}$

Continued

Chemical Method -

$$\text{Wt.\% HCHO} = \frac{3.0}{.5153} (0.9366 \times 50 - .0988 \times 19.5) = 16.21$$

$$\text{Wt.\% } CH_3COOH = \frac{6 \times .00967 \times 10.9}{0.2724} = 2.32$$

* One area unit = 10.55 $(\text{Centimeter})^2$

** The values inside parentheses are corrections based on Rosie' method (8).

Analysis of Liquid Product on Gas Chromatography

The wt. % of each liquid product was calculated by dividing its area to the total area of all components detected. The % area of each component is closer to its weight fraction than mole fraction in multicomponent mixture as shown in the following table:

A Sample Analysis

Component	Grams Mixed	Wt. %	Area %	Mole %
Acetone	.7856	8.76	9.16	3.495
Methanol	.9369	10.45	13.01	7.54
Isobutanol	.9099	10.11	9.81	3.18
N-butanol	.4535	5.06	5.01	1.585
H_2O	5.8786	65.58	63.01	84.2

Area was measured by planimeter.

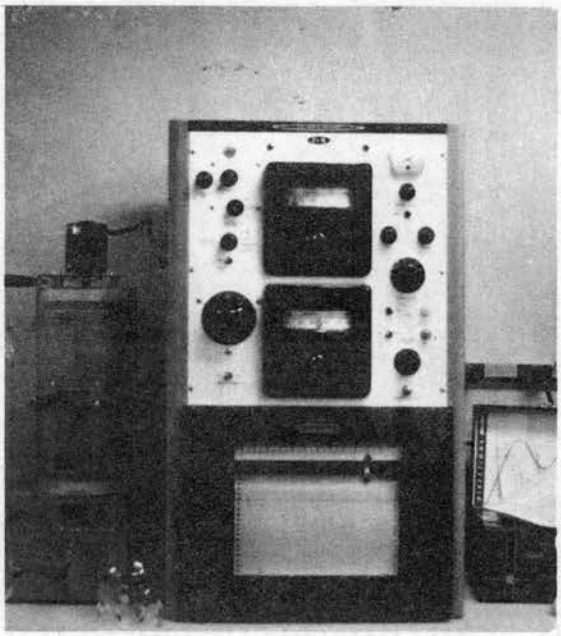

Figure 27

Programmed Gas Chromatography Unit

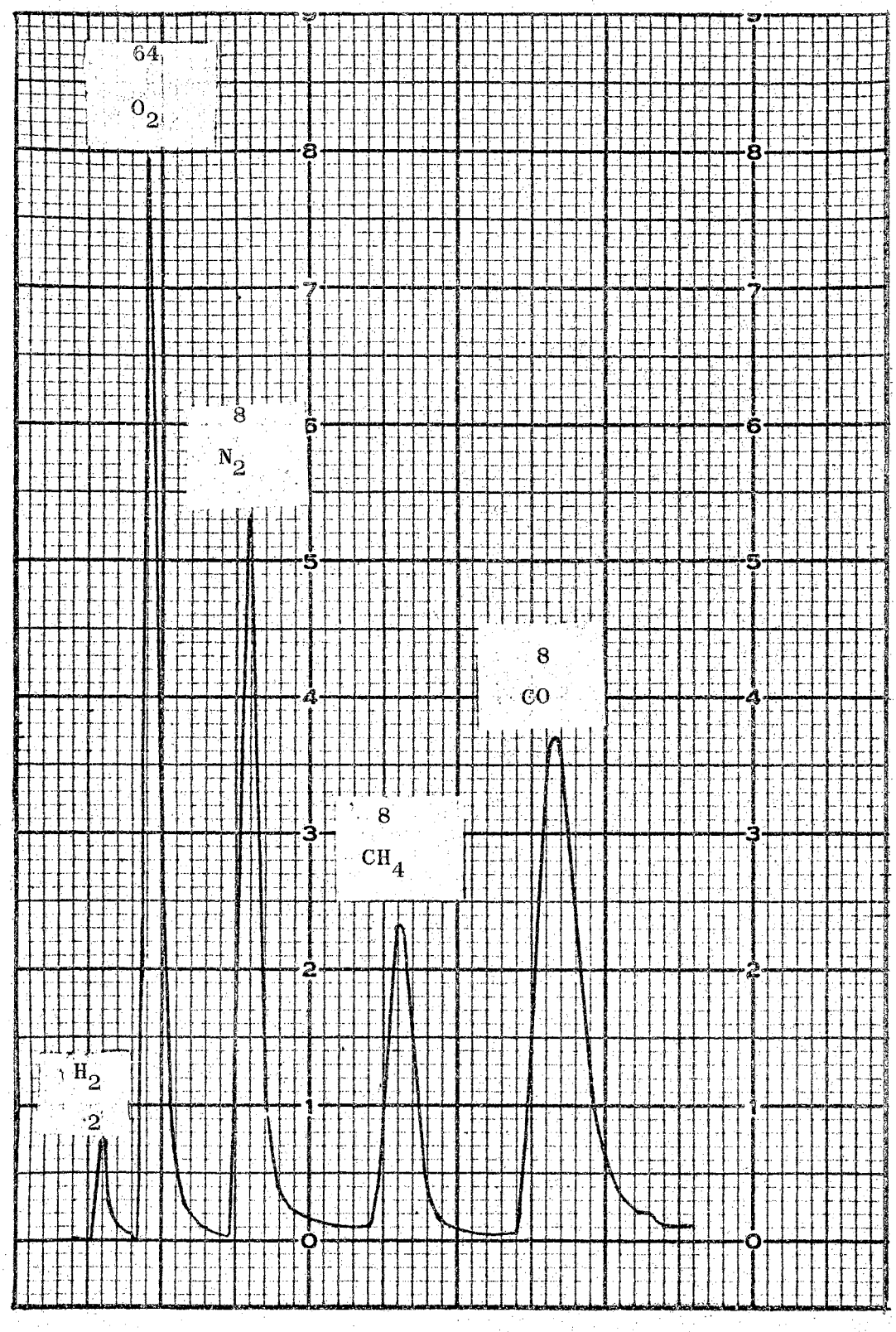

Figure 28

Molecular Sieve Column

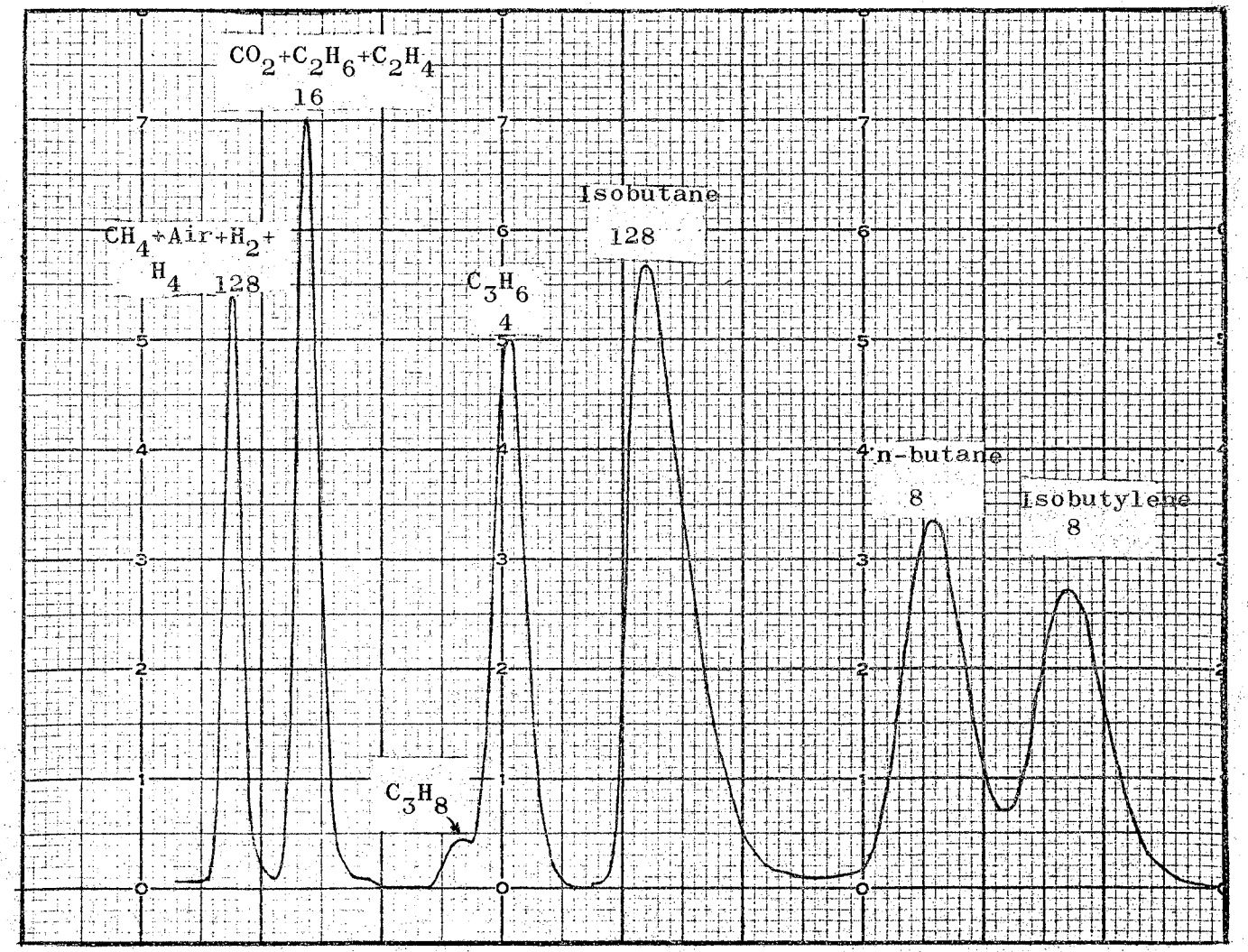

Figure 29

Di-Butyl Phthallate Column

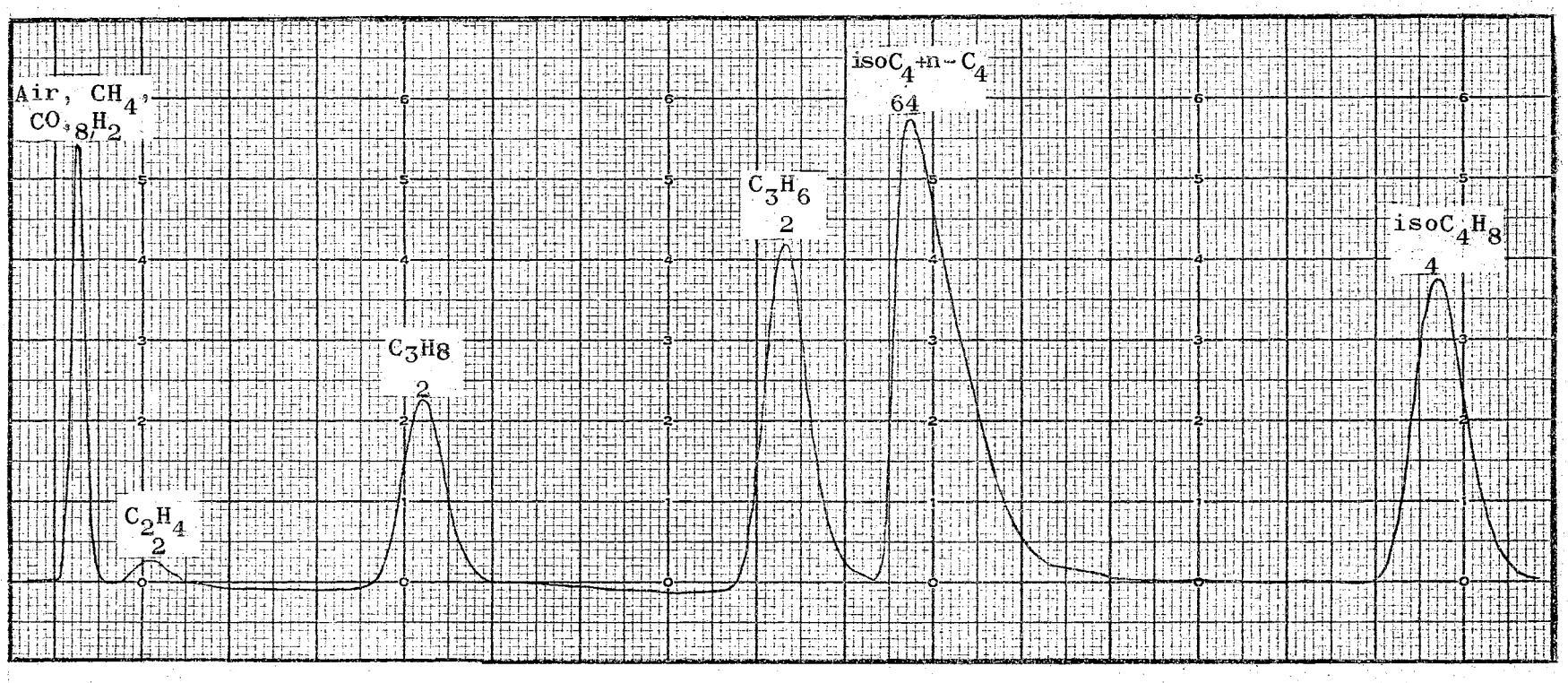

Figure 30

Activated Alumina Column

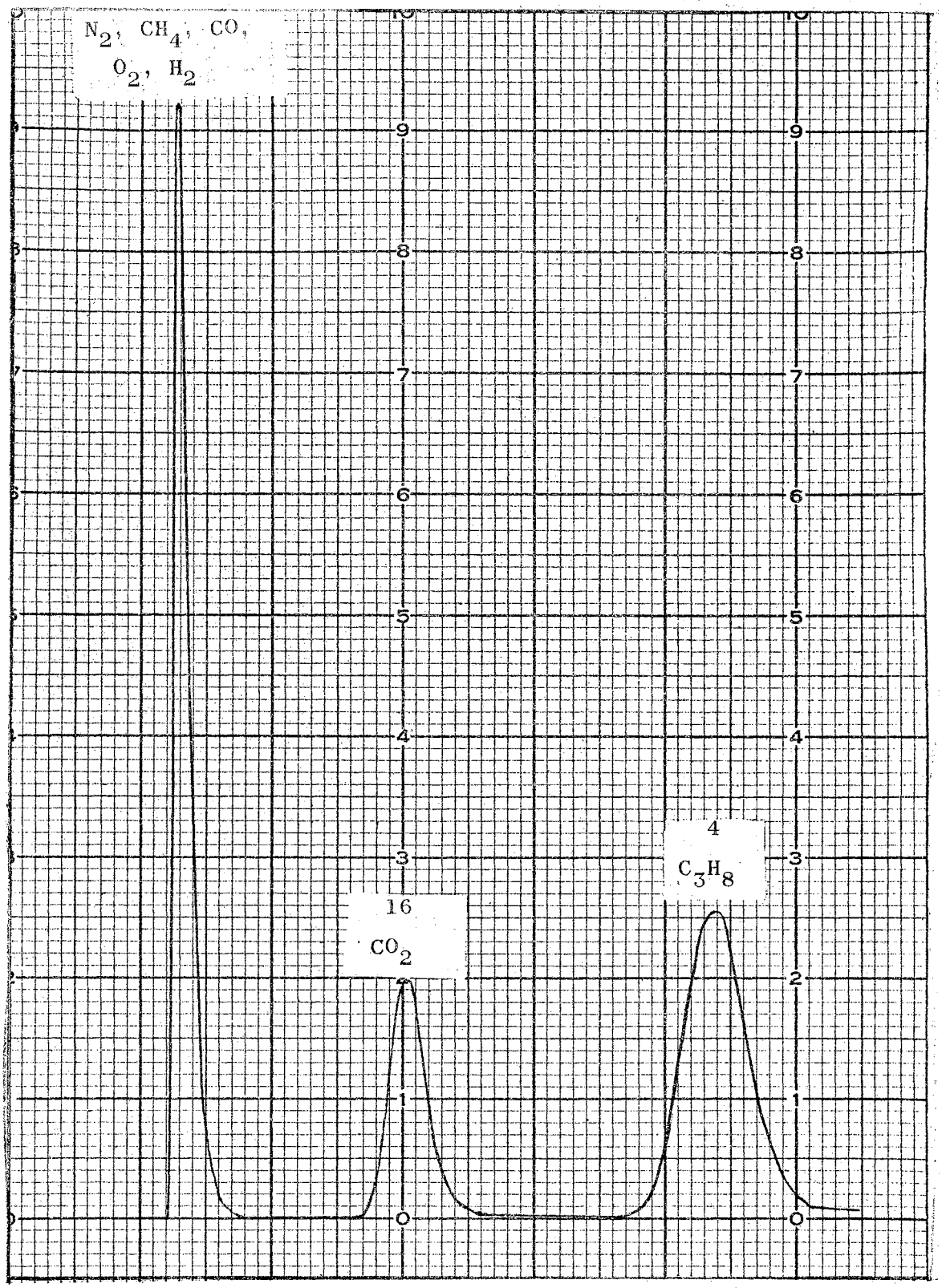

Figure 31

Silica Gel Column

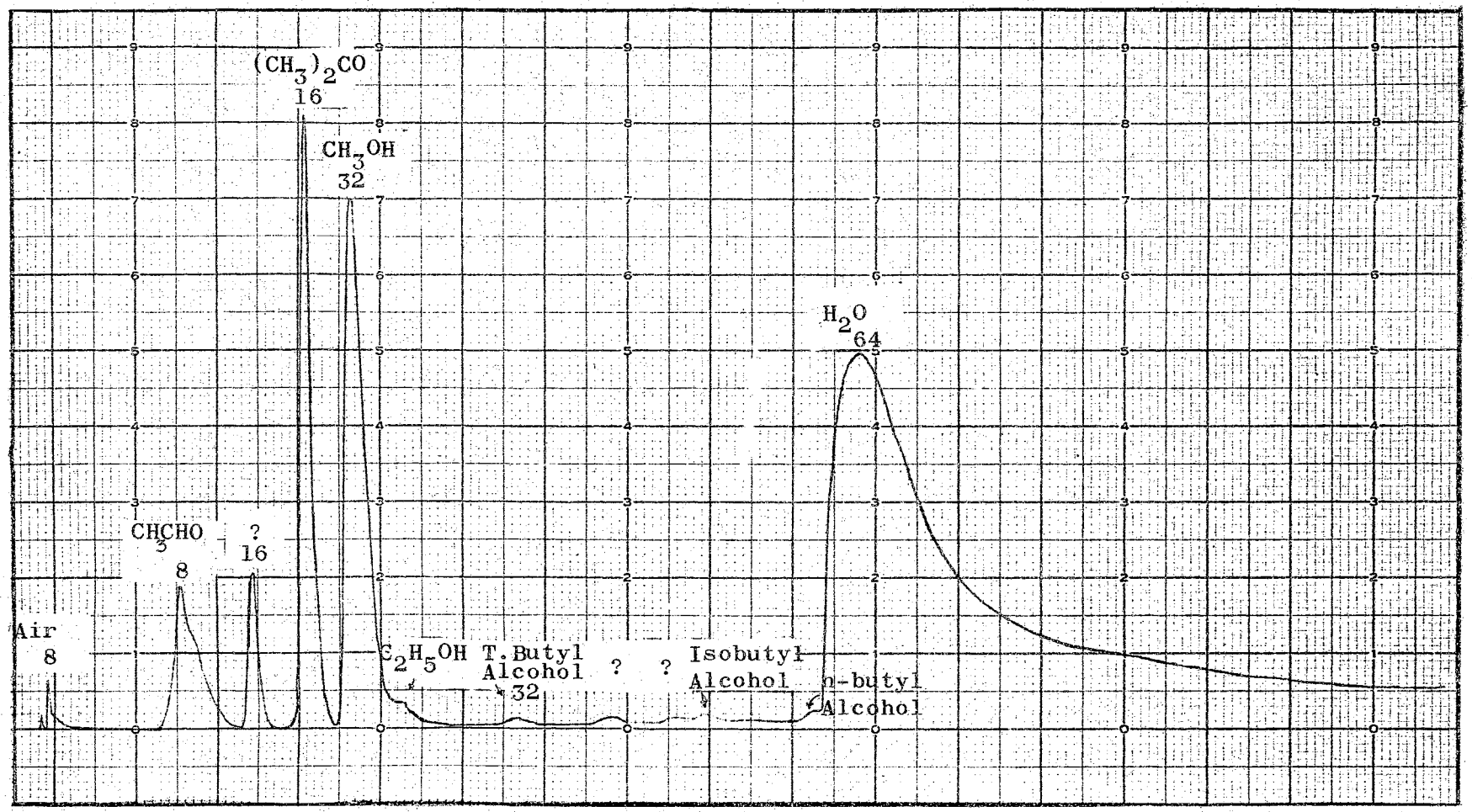

Figure 32

Di-n-Octyl Phthallate Column

APPENDIX V

NOMENCLATURE

A = frequency factor, $sec.^{-1}$

C_i = mole fraction of i component

E = total moles/hr. of gases leaving reactor

E = activation energy

k_i = rate constant of i_{th} reaction

k = overall reaction rate constant, $sec.^{-1}$

K' = kK in $\ln(\frac{1-qX}{1-X}) = K't$

ln = logarithm in the base e

$M = \frac{N^o_{isoC_4H_{10}}}{N^o_{O_2}}$

N^o_i = moles of i component fed to the reactor/hr.

N_i = moles of i component leaving the reactor/hr.

$q = \frac{\text{moles of isobutane converted/mole fed}}{\text{moles of oxygen converted/mole fed}}$

r = overall rate of reaction, $sec.^{-1}$

r_{max} = maximum rate of reaction

R = gas constant

t = time in seconds

T = absolute temperature, °K

X = moles of oxygen converted/mole fed

Y = moles of isobutane converted/mole fed

Greek Symbol

Θ = contact time, sec.

VITA

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Minor Field: Mathematics

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Professional Experience: Training at Abadan Refinery, Summers 1956 and 1957; Part-time assistant in a research project at the Engineering Field Station, University of California, February 1959-August, 1960.